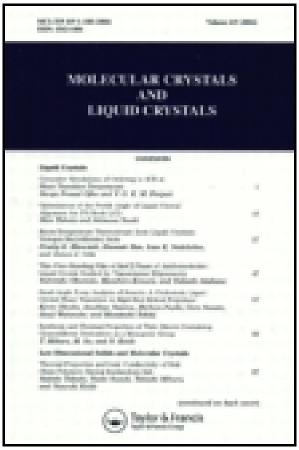

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Odile Fichet [a] , Jean-Philippe Bourgoin [b] , Pierre Delhaes [a] , Bernard Desbat [c] , Vassilis Gionis [a d] & Vyacheslay Yartsev [a e]

[a] CRPP CNRS, av. A. Schweitzer, 33600, Pessac, FRANCE

[b] CEA-IRF-DPhG-SCM, CEN Saclay, 91191, Gif-Sur-Yvette Cedex, FRANCE

[c] Laboratoire de Spectroscopie Moléculaire et Cristalline, Université Bordeaux I, 33405, Talence, FRANCE

[d] On leave from Theor. Phys. Chem. Institute NHSF, 116/35, Athens, GREECE

[e] On leave from Chelyabinsk State University, 454136, Chelyabinsk, RUSSIA

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SPECTROSCOPIC AND ELECTRONIC PROPERTIES OF CONDUCTING TCNQ LB FILMS ISSUED FROM A HOMODOPING STRATEGY

ODILE FICHET[1], JEAN-PHILIPPE BOURGOIN[2], PIERRE DELHAES[1], BERNARD DESBAT[3], VASSILIS GIONIS[1a] and VYACHESLAV YARTSEV[1b]
[1]CRPP CNRS, av. A. Schweitzer, 33600 Pessac, FRANCE
[2]CEA-IRF-DPhG-SCM, CEN Saclay, 91191 Gif-Sur-Yvette Cedex, FRANCE
[3]Laboratoire de Spectroscopie Moléculaire et Cristalline, Université Bordeaux I, 33405 Talence FRANCE
[a]On leave from Theor. Phys. Chem. Institute NHSF, 116/35 Athens, GREECE
[b]On leave from Chelyabinsk State University, 454136 Chelyabinsk, RUSSIA

Abstract We report the preparation and physical properties of Langmuir-Blodgett films obtained by mixing in the same layer neutral amphiphilic octadecyl tetracyanoquinodimethane (C_{18}TCNQ) and ionic semi-amphiphilic $(C_{18}S)_2$ dithiolium-TCNQ molecules. Cluster approach is used for the interpretation of electronic charge transfer band and vibronic features in infrared as a result of electron-molecular vibration coupling. The role of the in-plane long range order is discussed in view of increasing the d.c. conductivity value.

INTRODUCTION

In order to obtain a conducting LB film it is necessary to create a mixed valence system from electroactive molecular assemblies with amphiphilic character.[1] Among the different attempts the works using TCNQ salts and complexes have been the most developed ones with two main approaches.

In the first one a mixed valence state is obtained by a post-deposit doping with iodine of binary TCNQ salts which were not in this mixed valence state during the initial film preparation.[2] The second way (so-called homodoping strategy) employs a binary TCNQ salt which is homogeneously mixed in the spreading solution with a neutral alkyl TCNQ (C_{18}TCNQ).[3] It appears that the latter technique is a more general approach which allows to furnish a mixed valence state in many cases for different counter-ions even when the iodine doping process does not work.[4] Furthermore, it has been shown for the first time[3] that using the homodoping strategy one can obtain even conducting monolayer.

Following these tracks and looking for the influence of the counter-ion we have worked on a new series of $(C_{18}S)_2$dithiolium-TCNQ salts[5] which present some specific features. In contrast to sulphonium salts[3], where LB films of Y-type have been prepared, a non-centrosymmetric Z-type multilayered structure is obtained with $(C_{18}S)_2$dithiolium cation. In particular, it has been shown that the $(C_{18}S)_2$dithiolium-TCNQ salt which contains two alkyl chains on the dithiolium cation is insulating even after iodine doping.[5] It has been shown that this characteristics are related with a specific "sandwich-like" monolayer organization as shown by *in situ* ellipsometric and surface potential experiments.[6]

We have decided to extend the homodoping technique to this ionic semi-amphiphilic salt by mixing the liquid solution of $(C_{18}S)_2$ dithiolium-TCNQ with different amount of neutral C_{18}TCNQ. We play therefore with the mean degree of ionicity which should be in principle defined from the initial stoichiometry ratio[4] and also with the number of deposited layers as two primary independent parameters.

We will present in the next part the experimental conditions for getting such LB homodoped films together with their physical properties, i. e. optical absorption spectra and d. c. conductivity measurements.

Following our experimental results we propose in the third section a theoretical approach which is based upon the electron-molecular vibration (EMV) linear coupling model.[7] Finally, we shall compare the EMV coupling constants found for conducting films and charge transfer crystals and discuss the local description in the framework of our model and the general picture extracted from the d.c. conductivity experiments.

EXPERIMENTAL

LB film preparation

The charge transfer salt $(C_{18}S)_2$ dithiolium-TCNQ and the high purity C_{18}TCNQ are dissolved in chloroform ($c = 10^{-4}$ mol/l) and mixed together before spreading at the nitrogen-water interface (ATEMETA LB 105 trough). The *in situ* molecular organization of these mixed monolayers at the air-water interface has been investigated.[8] These observations have allowed us to conclude that we are dealing with homogeneous monolayers for $n \leq 3$. Besides, the *in situ* infrared spectra has demonstrated that mixed valence clusters are spontaneously formed at the water surface.

The samples of LB films have been prepared using the vertical dipping method on different hydrophilic substrates, usually CaF_2 and ZnSe for the optical experiments. In all cases the monolayer transfer has been of Z-type with a transfer ratio close to unity up to 100 deposits as already observed for the pristine TCNQ salt.[5]

We have measured a series of structural, optical and electronic properties using the already described technique.[9] The parameters at our disposal are the mixture composition $1{:}n$ with $0.5 < n < 3$ and the number of layers N which are deposited.

X-ray diffraction spectra

Although the X-ray diffraction bands 00l, where $2 \leq l \leq 5$, were broad and weak, they were detected in all samples. The thickness of every monolayer was found to be 36 ± 2 Å. Pure $(C_{18}S)_2$ dithiolium-TCNQ multilayers deposited at the pressure of 20 mN/m (area per aliphatic chain $A = 30$ Å^2) have the interlayer spacing of 23 Å only. Homodoped films are obtained at the pressure of 25 mN/m with smaller unit area $A = 25$ Å^2. A smaller area with a larger monolayer thickness in these homodoped films should correspond to the all-trans conformation of the aliphatic chains and to a few Angström shift of dithiolium ring from the layer surface leaving enough space for TCNQ molecule with its long axis parallel to the substrate. Such intralayer arrangement favours stacking of TCNQ molecules and eventually high electrical conductivity.

Visible and infrared absorption spectra

The selected room temperature spectra are presented in figures 1 and 2. Figure 1 shows the results obtained for a constant number of layers ($N = 50$) when the overall stoichiometry ($1{:}n$) is varied. We can distinguish two kinds of spectra:

i) for the mixture (1:0.5) we observe a charge transfer band at 8400 cm^{-1} which corresponds to a "B-type band" associated with transition in a fully ionized cluster as for example in a $(TCNQ^-)_2$ dimer. Indeed, this spectrum is reminiscent of the (octadecylphenathiolinium^{++}) $(TCNQ^-)_2$ salt [10] which presents both a charge transfer

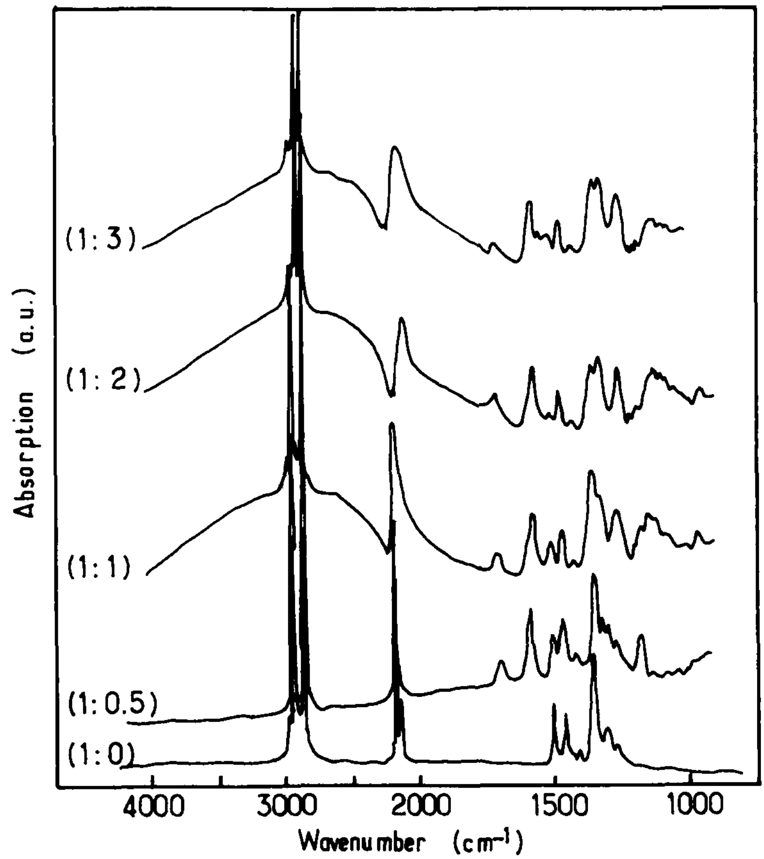

FIGURE 1 Infrared absorption spectra at 300 K of 50 layers of $[(C_{18}S)_2$ dithiolium-TCNQ$]_1$: $[C_{18}TCNQ]_2$ LB films built up with different stoichiometries

band around 9000 cm^{-1} and several vibronic bands located at 1575, 1351 and 1177 cm^{-1} for the totally symmetric (a_g) TCNQ modes ν_3, ν_4 and ν_5, respectively.

ii) for the other compositions we see immediately a "A-type" charge transfer band around 3000 cm^{-1}characteristic of a mixed valence system associated with several strong vibronic bands due to the excitation of intramolecular vibrations via the EMV coupling.[7]

These spectra appear rather similar to those already observed by Saclay's group[3] for sulphonium salts and besides they are not stoichiometry dependent. It turns out that we are in the presence of a fixed type of mixed valence cluster. So far we have not enough experimental evidence to conclude definitively which kind of molecular organization is realized, therefore we shall apply the formula valid for the single charge transfer excitation band both in dimers and trimers with its energy considered as an ajustable parameter.

Figure 2 shows the infrared absorption spectra for the classical stoichiometry (1:2) for different number of deposited layers on CaF_2 or ZnSe substrates. The fundamental observation is that we do not see any significant spectral changes with either the film thickness or the type of substrate. In order to check this point we have integrated the absorption of CH_3 and CH_2 stretching vibrations of alkyl chains between 2800 and

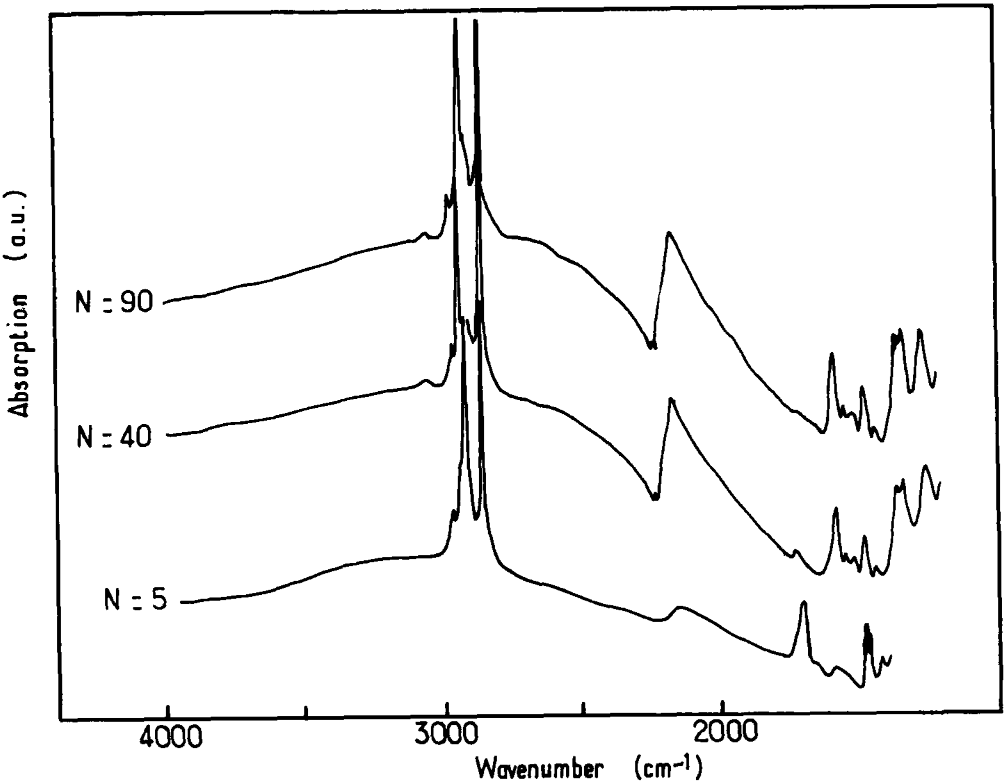

FIGURE 2 Infrared absorption spectra at 300 K of N layers of [$(C_{18}S)_2$ dithiolium-TCNQ]$_1$: [C_{18}TCNQ]$_2$ LB films deposited on CaF_2 substrate precoated with five layers of behenic acid

3000 cm^{-1} and we have found intensities values which are proportional to N, the number of Z-type deposited layers. In a complementary experiment we have also checked the existence of some in-plane linear dichroism associated with a possible molecular orientation as already found in similar materials.[11] However, our LB films appear as optically isotropic because the band intensities are constant as long as the electrical field lies in the layer plane.

From this data it appears therefore that the cluster theory, already developed for crystalline materials can be applied in order to interpret LB film results as well. We have selected one typical result representative of all experiments with n ≥ 1 (N = 50, stoichiometry 1:2) for applying the new fitting procedure presented in the next section.

d.c. electrical conductivity

Gold-palladium (80-20 %) electrodes were evaporated on the LB films deposited onto CaF_2 substrates for d.c. conductivity measurements employing as contacts aconducting paste on the base of colloidal graphite. The room temperature d.c. conductivity which is calculated using the full layer thickness can be increased by a factor of two if hydrophilic substrates without precoating are used. This conductivity rapidly deteriorates if the samples are left in ambient conditions unless they are kept cool under nitrogen atmosphere. As a function of composition a maximal conductivity ($\sigma \cong 10^{-2}$ S cm^{-1}) has

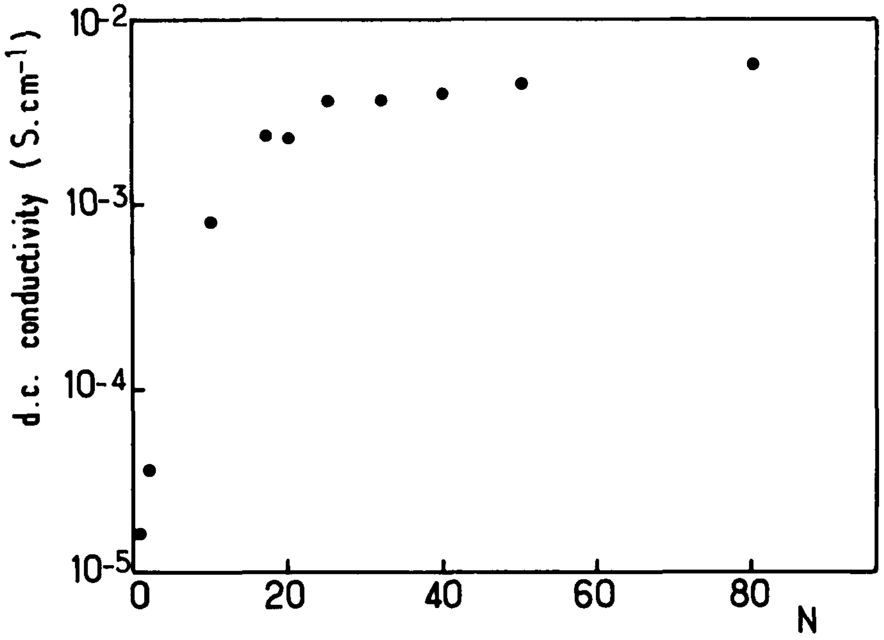

FIGURE 3 Electrical conductivity of $[(C_{18}S)_2$ dithiolium-TCNQ$]_1$: $[C_{18}TCNQ]_2$ LB film versus the number of layers (N)

been obtained for $n = 2$ and 3. For $n = 1$ the d.c. conductivity is five time smaller and for $n = 0.5$ the film is insulating.

In the temperature interval under investigation (150 - 300 K) the d.c. conductivity has a semiconducting behaviour with the activation energy $E_a = 0.2$ eV (for $n = 2$). The dependence of σ on the number of layers N is shown in Fig. 3. A rather sharp decrease of conductivity is observed as N goes down, but even for a single layer a finite value 1.5 10^{-5} S cm^{-1} has been detected.

DISCUSSION

The absorption spectra of LB films presented in Fig. 1 look very much like the spectra of quasi-1D molecular crystals where the molecules are arranged to form linear clusters of 2, 3 and 4 units. It means that the optical properties of both LB films and crystals are determined by rather small molecular clusters in accordance with a higher degree of electron localization in these compounds compared to "classic" semiconductors, such as Ge or Si. The physical reason for such behaviour is discussed elsewhere.[12]

The simplest expression for the complex conductivity of an assembly of linear clusters with at least two molecules has the form [12]

$$\sigma(\omega) = -\,i\,\omega N_c \frac{e^2a^2}{4} \frac{1}{\frac{1}{\chi(\omega)} - D(\omega)} \qquad (1)$$

where

$$\chi(\omega) = \frac{2\,M^2\,\omega_{CT}}{\omega_{CT}^2 - \omega^2 - i\,\omega\,\Gamma} \tag{2}$$

$$D(\omega) = \sum_\alpha \frac{g_\alpha^2\,\nu_\alpha}{\nu_\alpha^2 - \omega^2 - i\,\omega\,\gamma_\alpha} \tag{3}$$

Here N_c is the number of clusters per unit volume, a denotes the distance of charge transfer, M is the matrix element for the electronic excitation with the energy ω_{CT} ($\hbar = 1$) and phenomenological damping Γ, g_α denotes the EMV coupling constant for an intramolecular vibration ν_α with a natural width γ_α. The sum in Eqn. (3) is taken over all the vibronic modes linearly coupled to electronic charge transfer excitation.

Firstly, we discuss electronic charge transfer bands. The so-called "B-band" at 8500 cm^{-1} in (1:0.5) sample indicates the presence of quasi-isolated dimers with two electrons in this LB film, while charge transfer energy around 2100 cm^{-1} for other stoichiometries points to dimers with one electron. From these two characteristics one can estimate transfer integral $t = 1050\ \mathrm{cm}^{-1}$ and Coulomb repulsion energy $U = 8000\ \mathrm{cm}^{-1}$. Hopping mechanism of d.c. conductivity in charge transfer organic compounds predicts[13] an activation energy 0.2 eV found as the energy required for interdimer transition $(\mathrm{TCNQ}_2)^- + (\mathrm{TCNQ}_2)^- \Rightarrow (\mathrm{TCNQ}^-)_2 + (\mathrm{TCNQ}_2)^0$. This value agrees with the one found experimentally.

Broad asymmetric bands at 2173, 1575, 1328 and around 1100 cm^{-1} are attributed to the excitation of totally symmetric modes of TCNQ molecule via EMV coupling. In the case when vibronic bands are not close to each other, several simple relations between g_α and the position of vibronic band in the spectrum of the real part of the conductivity have been offered. They are widely used in interpretation of reflectance data which can be transformed into conductivity spectra by Kramers-Kronig procedure. Unfortunately, for LB films only absorption spectra are observed and vibronic bands in these spectra have positions different from those in conductivity due to frequency dependent function relating these two characteristics. Our investigation[14] of absorbance expression gave the relation between EMV coupling constants g_α, positions of vibronic bands in absorbance Ω_α and in Raman spectrum ν_α:

$$g_\alpha^2 = \frac{\omega_{CT}\,\nu_\alpha}{2M^2}\left(1 - \frac{\Omega_\alpha^2}{\nu_\alpha^2}\right)\left(1 - \frac{\Omega_\alpha^2}{\omega_{CT}^2} + \frac{\Gamma\Omega_\alpha}{\sqrt{3}\,\omega_{CT}^2}\right) \tag{4}$$

The values of g_α obtained by Eqn. 4 are given in Table 1. However, it has been shown[14] that the interaction between vibrations via coupling to common electronic excitation results in the increase of intensity of low-frequency band and the shift of this band to lower frequency, while the opposite is observed for the high frequency band.

It has been argued[15] that the attachment of $\mathrm{C}_{18}\mathrm{H}_{37}$ chain to a TCNQ molecule does not change vibrations which do not involve the motions of C-H bond in TCNQ, but $a_g\nu_5$ vibration can excite vibrations of $\mathrm{C}_{18}\mathrm{H}_{37}$ chain. Such a two-step vibrational coupling was able to explain unusual fine structure of $a_g\nu_5$ band and mathematically this extention is described by the following modification of Eqn. (3):

$$D(\omega) = \sum_\alpha \frac{g_\alpha^2\,\nu_\alpha}{\nu_\alpha^2 - \omega^2 - i\,\omega\,\gamma_\alpha - \sum_\beta \dfrac{k_{\alpha\beta}^2\,\nu_\alpha\,\omega_\beta}{\omega_\beta^2 - \omega^2 - i\,\omega\,\gamma_\beta}} \tag{5}$$

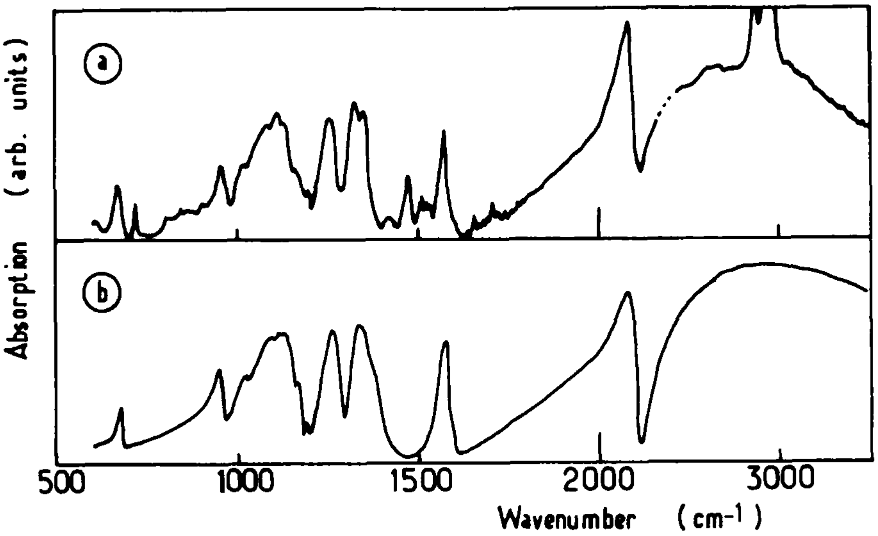

FIGURE 4 Experimental (a) and calculated (b) absorption spectra of $(C_{18}S)_2$ dithiolium-TCNQ$]_1$: $[C_{18}TCNQ]_2$ LB film.

where ω_β and γ_β denote frequency and damping constant for β-vibration of $C_{18}H_{37}$ chain and k_{5b} is the "TCNQ-$C_{18}H_{37}$ chain" coupling constant.

The fit of Eqns. (1,2 and 5) to the experimental absorbance of $[(C_{18}S)_2$dithiolium-TCNQ$]_1$: $[C_{18}TCNQ]_2$ LB film is shown in Fig. 4. The parameters of electronic subsystem are $\omega_{CT} = 2100$ cm^{-1}, $\Gamma = 2000$ cm^{-1}, $M = 1$. The EMV coupling constants g_α are given in the fifth column of Table 1 and the frequencies ν_α are taken as observed experimentally in Raman spectrum of $C_{18}TCNQ$ (column 3 in Table 1). The frequencies ω_β are 1261, 1190, 1163, 1126, 1106 and 1028 cm^{-1} with corresponding values of $k_{5\beta}$: 100, 15, 15, 10, 15 and 30 cm^{-1}. The damping factors γ_α and γ_β are chosen for all modes equal 10 cm-1.

Finally, it follows from Table 1 that the EMV coupling constants are similar to those obtained for 2:1 TCNQ crystalline salts.[7] These values are molecular characteristics

TABLE 1 Observed and calculated frequencies of some $C_{18}TCNQ$ vibrations, vibronic bands in $[(C_{18}S)_2$dithiolium-TCNQ$]_1$: $[C_{18}TCNQ]_2$ LB film and EMV coupling constants

$TCNQ^0$	$C_{18}TCNQ$		[DT-TCNQ$]_1$: $[C_{18}TCNQ]_2$		MEM-$TCNQ_2$
ν_α/cm^{-1} Raman[16]	ν_α/cm^{-1} Calc.[17]	ν_α/cm^{-1} Raman[17]	g_α/cm^{-1} Eq.(4)	g_α/cm^{-1} fit in Fig. 4	g_α/cm^{-1} Ref. 7
2229	2231	2226	253	350	350
1602	1590	1607	256	400	540
1454	1461	1455	497	560	500
1207	1208	1214	414	280	300
948	950	961	80	85	85
711	-	679	106	100	190

and therefore this comparison supports our assumption about the formation of mixed valence dimers in homodoped LB films with $n \geq 1$. Strictly speaking, in the case of LB films issued from a Z-type deposit we can not be in presence of a centro-symmetrical dimer. It turns out therefore that the EMV coupling in the homodoped LB films is taking place as if TCNQ molecules were without attached $C_{18}H_{37}$ chains for all a_g modes of parent TCNQ molecule except ν_5. In the latter case we observe a two-step excitation of vibrations of $C_{18}H_{37}$ chain.

CONCLUSIONS

A comparison between the optical data and the d.c. electrical conductivity can be used for a discussion of the role of disorder in LB films. The optical conductivity calculated[14] for the parameters ω_{CT} and Γ of electronic charge transfer excitation obtained from the fit in Fig. 4 is about 100 S cm^{-1} at the room temperature. This is the upper value following from Drude model. The descrepancy with the observed value of the d.c. conductivity can be explained both by explicit introduction of electronic correlations in strongly dimerized stacks (e.g. employing the Hubbard model) and/or by considering the statistical disorder with only a short range order. It appears therefore that to increase the d.c. electrical conductivity it will be necessary to improve the in-plane long range order with a quasi-regular stacking of TCNQ molecules.

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