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Conducting Langmuir–Blodgett films of heptadecylcarboxymethyl-BEDT-TTF

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Abstract

Surfactant compounds containing the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) donor group appeared to be very promising for production of highly conducting Langmuir–Blodgett (LB) films. A new donor compound, i.e. heptadecylcarboxymethyl-BEDT-TTF, is used to increase interaction of the molecules with water. It possesses donor properties of hexadecyl-BEDT-TTF and contains a strong hydrophilic group which does not prevent close packing of BEDT-TTF fragments due to its small dimensions. As a result, uniform highly conducting LB films of heptadecylcarboxymethyl-BEDT-TTF are deposited from the water subphase containing $FeCl_3$. Conductivity of the films reaches 4 $ohm^{-1} cm^{-1}$. Electron and small-angle X-ray diffraction studies are carried out. Some structure parameters are determined. Proceeding from these data possible structure models are proposed and peculiarities of the structure are discussed. The films are sensitive to the effect of electron beam and lose conductivity under irradiation. Thus, a desirable insulating pattern can be created in the conducting material which is important for technological applications.

Keywords: Langmuir–Blodgett films; Films; Bis(ethylenedithio)tetrathiafulvalene

1. Introduction

The search for new surfactant compounds suitable for producing conducting Langmuir–Blodgett (LB) films on the basis of charge-transfer complexes and salts [1–4] seems to be the first step to make possible their application in molecular electronics. It has been shown that some technological processes are applicable to films of such a type [5,6] and effects for device operation have already been discovered [7,8]. However, the procedures of functional element preparation are usually complicated and the results are poorly reproducible. Thus, for real applications the technology must be simplified as much as possible.

Surfactant compounds containing the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) donor group appeared to be very promising for production of highly conducting LB films. One inadequate feature of such compounds studied up to now is non-satisfactory surface activity resulting in poor spreading of the monolayers at the air–water interface and poor morphology of the deposited films. The idea to synthe-

size a compound similar to heptadecylcarboxymethyl-BEDT-TTF arose after studying the monolayers and LB films of several surfactant molecules with structures like that of hexadecyl-BEDT-TTF, but containing considerable changes in donor group [6] and the mixtures of these compounds containing small amounts of highly surface-active acceptors [6,8]. The last approach provided strong interaction of acceptor molecules both with water and donor molecules, which improved monolayer spreading. Another conclusion has been made that the BEDT-TTF fragment is the most suitable for obtaining a high value of conductivity. To avoid the use of mixtures of donor and acceptor molecules for improvement in spreading, the structure of the donor molecule should be modified for the purpose of increasing the interaction between the surfactant molecules and water. However, changes of transverse dimensions of the resultant molecule must not be strong because, in the other case, close packing of BEDT-TTF fragments and high conductivity of the film will be impossible. The best way is to include some atoms forming strong hydrogen bonds with water into the chain near the BEDT-TTF group. An additional requirement consists in the creation of a short bridge of $-CH_2-$ groups between the hydrophilic and donor fragments to avoid the considerable influ-

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ence of the hydrophilic group on the donor properties of the BEDT-TTF molecule.

The heptadecylcarboxymethyl-BEDT-TTF molecule with the formula:

$$C_{17}H_{35}-\underset{O}{\overset{\text{}}{C}}-O-CH_2 \quad \text{[BEDT-TTF structure]}$$
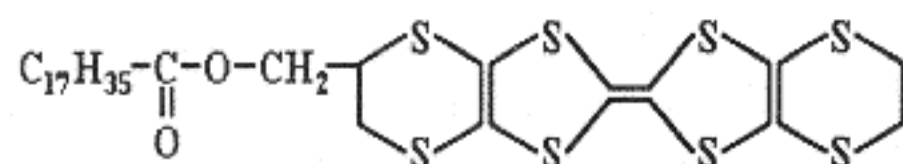
is an example to realize this idea. The –COO– group forms strong hydrogen bonds with water molecules and does not prevent close packing of BEDT-TTF fragments because of its small dimensions.

The main goal of the present work was to obtain uniform conducting LB films from the synthesized molecules. The experiments which were carried out to study the monolayers at the air–water interface and deposited multilayers showed that our reasonings concerning the proposed molecular structure appeared to be true and that the use of donor–acceptor mixtures for preparation of high quality conducting LB films is not obligatory. An electron diffraction study of the films was also carried out. Some structure parameters are determined and possible models of molecular packing are proposed. X-ray small-angle scattering experiments were fulfilled to determine the thickness of monolayer. The films of heptadecylcarboxymethyl-BEDT-TTF, similar to those of hexadecyl-BEDT-TTF, are sensitive to the effect of electron beam and lose conductivity under irradiation. The sensitivity of the films to the electron beam effect is evaluated.

2. Experimental

Synthesis of the heptadecylcarboxymethyl-BEDT-TTF molecule has already been published in a separate communication [9]. Purity of the compound used was better than 99.8%. Study of monolayers at the air–water interface and deposition of LB films was carried out with the LB–MDT system (Russia). A JEM-100C microscope (Japan) was used for electron microscopy and electron diffraction investigations. Small-angle X-ray diffraction patterns were measured with an AMUR-K diffractometer (Russia). Control of the film deposition quality was performed with an optical microscope at magnifications up to 800. An electron gun providing a wide electron beam with a density of 10^{-6}–10^{-5} A cm^{-2} at accelerating voltages from 1 to 3 kV installed in a chamber of a JEE-4C vacuum evaporator (Japan) was used for irradiation of the films. To destroy the conductivity, irradiation was produced with a dose in the range of 10^{-5}–10^{-3} C cm^{-2}.

The experimental work with the new compound consisted in optimization of the conditions of film deposition and in the choice of the best combination of the solvents to improve spreading. The influence of conditions of deposition on the properties of LB films was checked after every variation by optical and electron microscopy techniques. Conductivity was also measured. To form a charge-transfer salt with donor

molecules which is also necessary for the appearance of conductivity through closely packed BEDT-TTF stacks, the water subphase containing FeCl$_3$ was used. Charge-transfer salt formation is based in this case on the capability of ferrous ions to transfer from the Fe^{3+} state into the Fe^{2+} one. Electron probe analysis carried out in [10] for hexadecyl-BEDT-TTF films deposited from a similar subphase showed that donor molecules form a charge-transfer salt with ferrous ions which also includes hydroxyl ions.

It appeared that the best conditions of film formation are approximately the same as in the case of producing high quality hexadecyl-BEDT-TTF LB films with small additions of heptadecyloxycarbonyltetracyanoanthraquino-dimethane [6,8,10]. Thus, a mixture of hexane and chloroform in the ratio of 2 to 1 was used as a solvent; deposition was carried out by a vertical lift technique from the surface of a 10^{-4} M water solution of FeCl$_3$ and at pH 3.8. Surface pressure was supported at 28–35 mN m^{-1}; the speed of deposition was equal to 0.5–1 cm min^{-1}. To control the film morphology and uniformity, 10 to 50 monolayers were deposited onto silicon hydrophobic substrates for optical study and 11 to 31 monolayers were deposited onto copper grids covered by super-thin collodion films for electron microscopy and electron diffraction investigations.

LB films with gradually increasing thickness were deposited onto sapphire substrates with (evaporated beforehand) two overlapping systems of chromium electrodes with gaps of 50 μm to measure conductance by the two-probe technique. Details of such measurements and the approach used for evaluation of the chromium electrode, LB film junction resistance, thickness of conducting areas, as well as distribution of current along the normal to the layer plane, have been published elsewhere [10].

3. Results and discussion

First of all, we note that formation of uniform stable monomolecular layers of heptadecylcarboxymethyl-BEDT-TTF at the air–water interface appeared to be successful due to strong interaction of the molecules with water. As a result, uniform conducting LB films have been deposited. The value of conductivity obtained shows that the close packing of BEDT-TTF fragments is not disturbed due to chemical modifications made. These results are discussed in more detail in Sections 3.1, 3.2 and 3.5. An attempt to find a structure model which satisfies the electron diffraction and X-ray small-angle diffraction data is made in Sections 3.3 and 3.4.

3.1. Spreading of the monolayer at the air–water interface

The surface pressure–area isotherm of the monolayer (Fig. 1) gives an area per molecule of 0.35 ± 0.01 nm^2. The extrapolation of the isotherm to zero surface pressure was carried out for the interval between 25 and 42 mN m^{-1} because, at higher values of pressure, the curve of the isotherm changes
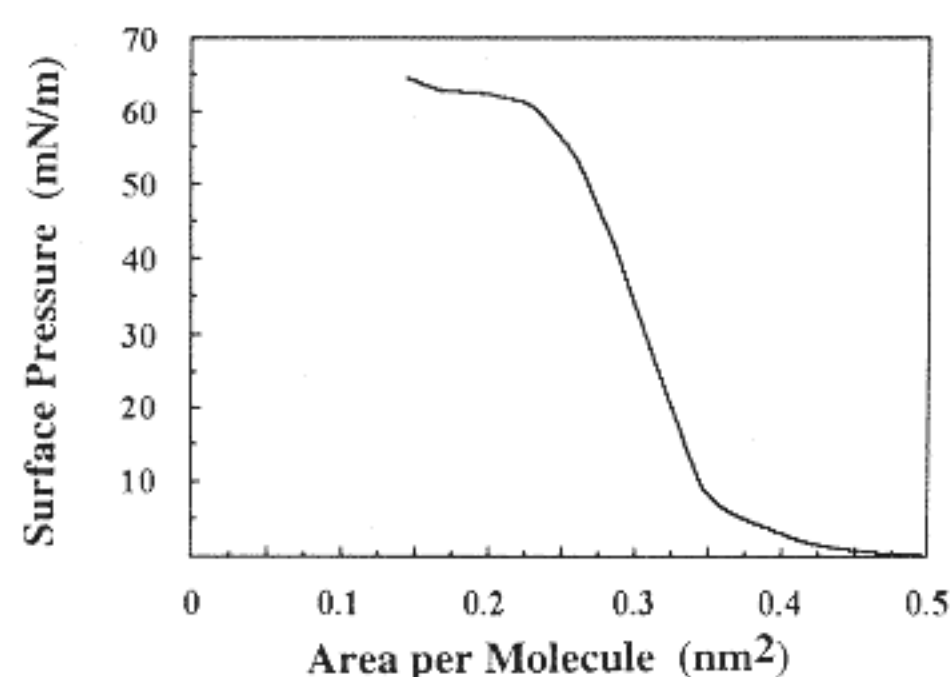
Fig. 1. Surface pressure–area isotherm of the heptadecylcarboxymethyl-BEDT-TTF monolayer at pH of 3.8 and 10^{-4} M concentration of $FeCl_3$.

as the result of the start of a slow collapse. Comparison of this value with the area per molecule in the layer plane calculated from the dimensions of the unit cell (0.342 ± 0.005 nm^2), which can be determined from electron diffraction data discussed below, shows that they practically coincide and, for this reason, the spreading of the compound at the air–water interface is very good, contrary to that of hexadecyl-BEDT-TTF monolayers [11], which form layers with average thickness approximately 1.3 times more than that of one monolayer. For example, if we suggest that defects arising after solvent evaporation are three monolayers thick, then initially before deposition 15% of the hexadecyl-BEDT-TTF monolayer area is defective. In reality this value is somewhat less because thicker defects containing other odd numbers of monolayers also arise.

3.2. Morphology of the LB films

Under the optimal conditions described above, uniform LB films with morphology similar to that of usual multilayers of fatty acid salts may be deposited. At least, when observing with an optical microscope the interference colours of the films with different thicknesses deposited on silicon substrates, practically no non-uniform areas can be detected in spite of the fact that artificially created steps of one bilayer thickness are distinguished easily. Only very rarely do the smallest bulk crystallites of 1–2 μm size with a density of approximately 2×10^4 cm^{-2} appear. Electron micrographs in this case show only a smooth surface because of the small dimensions of the crystallites (see below) and the impossibility of morphology observation at high magnifications, since destruction of the film takes place under irradiation by an electron beam of high density. Study of hexadecyl-BEDT-TTF film morphology, for example, with an optical microscope under the same conditions shows quite non-uniform surface. Variations of the multilayer thickness in different places of the substrate reach 15–20 nm when a film 60–70 nm thick is deposited. Such non-uniform areas can be easily observed also with an electron microscope under low magnifications [11].

3.3. Preliminary data on the film structure

The value of area per molecule (0.35 nm^2) gives the possibility of evaluating roughly the tilts of hydrocarbon chains and axes of BEDT-TTF groups to the plane of the substrate, as well as the thickness of the heptadecylcarboxymethyl-BEDT-TTF monolayer. Such preliminary calculations will help us later (Section 3.4) to choose correctly the unit cell because electron diffraction data in this case cannot be interpreted in a single manner.

We proceed here from the principle of close packing of molecules [12]. Since the molecule can easily change conformation due to rotations around single bonds located near the head, close packing must take place for both heads and tails. In another case, the energy of molecular interaction will decrease strongly because the dispersion interaction of both mentioned groups with neighbouring molecules is considerable. The area per one chain for different structures in the plane normal to the chain axis varies from 0.185 to 0.205 nm^2 according to data from the literature. It is clear that under such conditions interdigitation of the tails [13] is impossible. Thus, the angle between the hydrophobic tail axis and normal to the substrate surface in our case is equal to 53–57°.

The packing coefficient of BEDT-TTF groups can be adopted to be equal to 0.65–0.7 which is usual for aromatic systems. This coefficient is determined as a ratio of group volume with the atom radii equal to the van der Waals ones to the volume occupied by the group in the unit cell. Estimation of the angle between the BEDT-TTF axis and normal to the layer plane gives the value of 25–31°. Under these conditions the thickness of the monolayer equals 2.64–2.87 nm. We used for these calculations the values of head and tail lengths as 1.43 and 2.74 nm, respectively, with the boundary between them at the highest carbon atom of the BEDT-TTF fragment. Decrease of monolayer thickness due to packing of neighbouring layers of approximately 0.8–1.0 nm was taken into account as well.

Here and in the discussion below we suppose that ferrous ions are located somewhere between the monolayers and do not increase the thickness of the latter. This supposition seems to be reasonable because, according to the data of [10] for the films of hexadecyl-BEDT-TTF with the same conductiv-
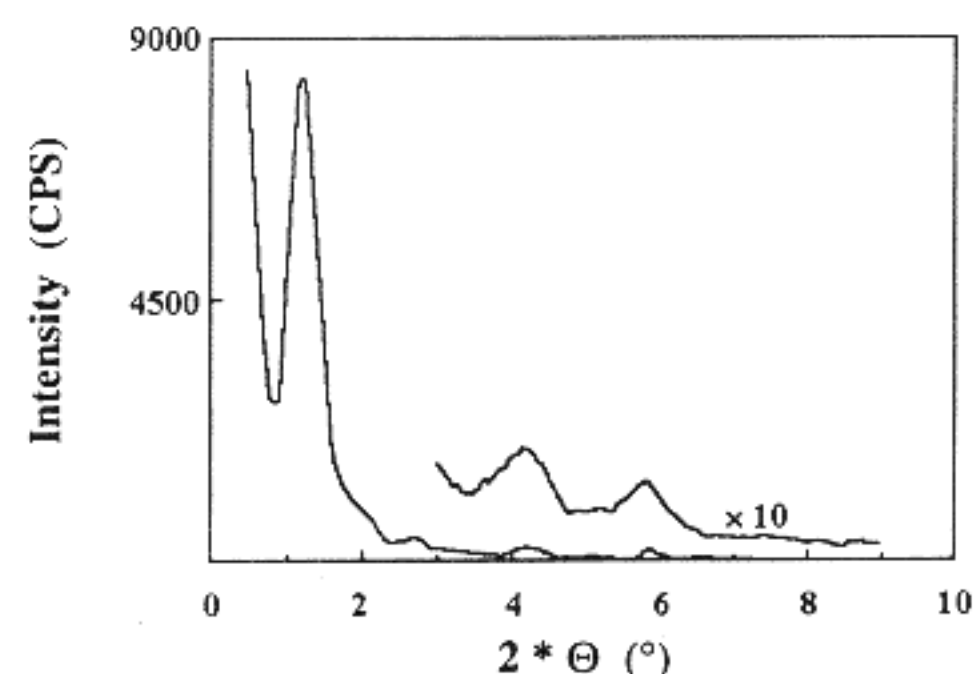

Fig. 2. Small-angle X-ray diffraction pattern of 40 monolayers of heptadecylcarboxymethyl-BEDT-TTF deposited from 10^{-4} M $FeCl_3$ solution at pH 3.8.
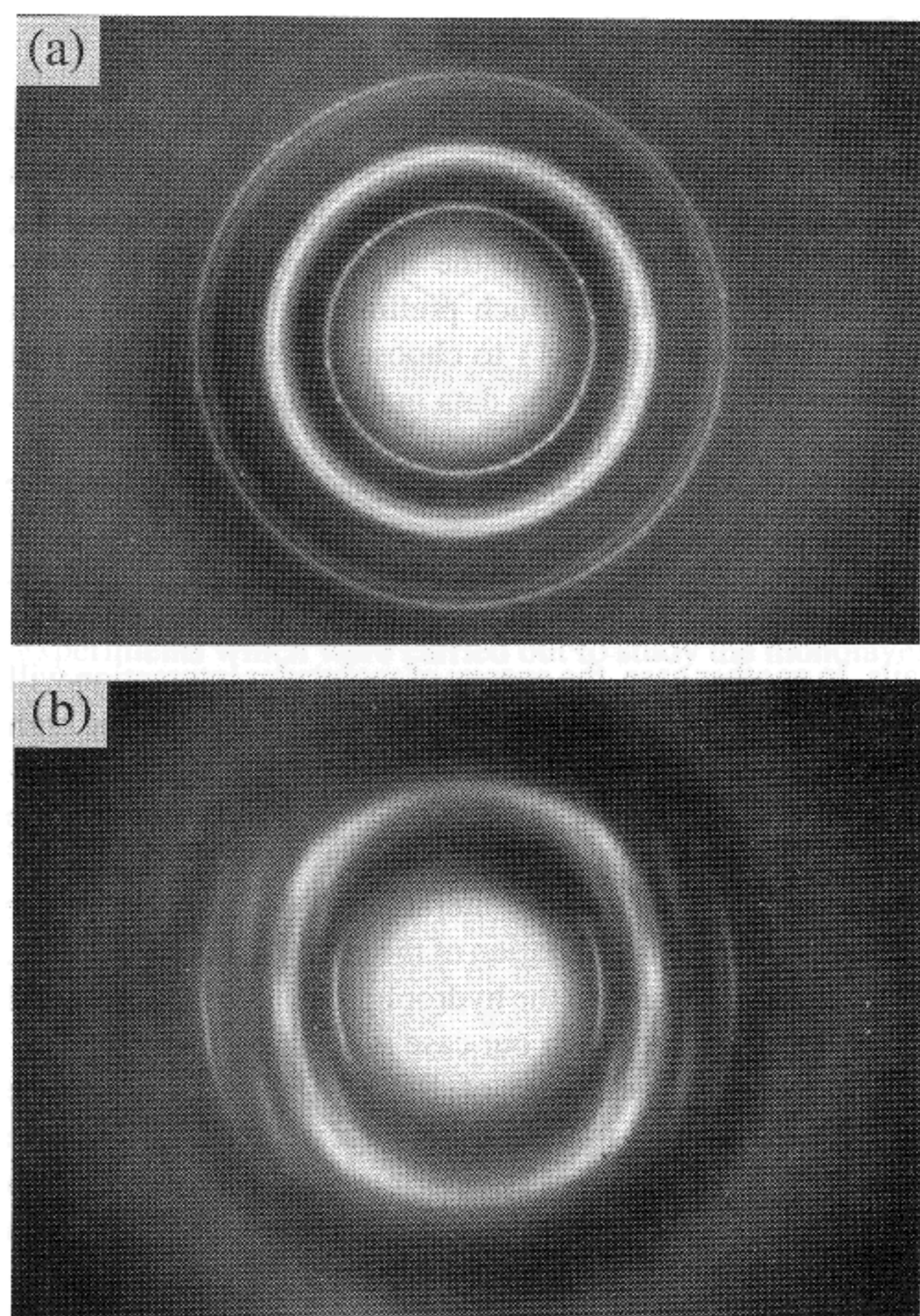
Fig. 3. Electron diffraction patterns of 19 monolayers of heptadecylcarboxymethyl-BEDT-TTF deposited from 10^{-4} M $FeCl_3$ solution at pH 3.8 for tilt angles of 0° (a) and 55° (b).

Table 1

Spacings d_{hk0} in the crystalline structure of the LB film of the heptadecyl-carboxymethyl-BEDT-TTF charge transfer salt

d_{hk0} (nm)	hk		
	Variant I	Variant II	Variant III
0.730	11	$2\bar{1}$	20
0.611	$\bar{2}1$	$\bar{1}2,02$	12,21
0.538	30	$\bar{2}2,30$	$\bar{2}2$
0.472	$\bar{3}1$	31	$\bar{3}1,03,\bar{1}3$
0.440	31	$\bar{3}2$	13,31
0.420	$\bar{1}2,02$	$\bar{1}3,03$	$\bar{3}2,\bar{2}3$
0.380	$\bar{4}1$	13,32	23,32
0.317	32,50	$\bar{4}3,42,50$	33
0.306	$\bar{4}2,\bar{5}1$	$\bar{2}4,04,33$	$\bar{4}3,\bar{3}4$

ity, only one ion is coordinated with five to nine molecules. The small-angle X-ray diffraction pattern (Fig. 2) shows the period of 5.86 ± 0.18 nm. Comparison with the monolayer thickness evaluated previously indicates that the period value is equal to the bilayer thickness and proves the possibility of using the area per molecule obtained from the surface pressure–area isotherm as the basic value for interpretation of the electron diffraction results.

In spite of the tails being tilted strongly to the layer plane, the collapse pressure of the order of 55–60 mN m^{-1} is rather high and the stability of the monolayer is satisfactory up to a surface pressure of 37–40 mN m^{-1}. At a value of surface pressure of approximately 30 mN m^{-1}, for example, the decrease of monolayer area equals about 5–7% per hour. We consider this fact as a result of the strong interaction of heptadecylcarboxymethyl-BEDT-TTF molecules with water due to formation of hydrogen bonds.

3.4. Model of crystalline structure

Electron diffraction patterns (Fig. 3) show that the crystallites form texture with the axis normal to the substrate plane and arbitrary orientation of the latter in the azimuthal direction. The mosaic angle is equal to 5–7°. Crystalline order in the normal direction is very poor. It is more probable that the arrangement of the neighbouring bilayers is not correlated in practice. Dimensions of the crystallites in the substrate plane are equal to 30–40 nm. Although arcs corresponding to hkl reflections with $l \neq 0$ are not resolved in the electron diffraction pattern in Fig. 3(b) it is possible to determine a, b and γ parameters of the unit cell with adequate accuracy. The point is that the period along the normal to the layer plane is at least 3.5 times more than the two other periods. Thus, irrespective of the type of unit cell, $hk0$ reflections with small h and k indices are located near Ewald's sphere. Simple estimations show that in spite of the fact that some rings in Fig. 3(a) may be formed by the reflections with $l \neq 0$, under such conditions in the worst case the difference between the spacings d_{hk0} and the above-mentioned spacings d_{hkl} cannot be more than 1.3%. However, all variants of the unit cells obtained within this accuracy of coincidence of the experimental and calculated spacings must be considered as probable, regardless of different errors of determination of the parameters. According to this conclusion, d_{hk0} spacings can be determined from the electron diffraction pattern in Fig. 3(a) within an accuracy of 1.3%. Three different variants of the C face of the unit cell are possible under such a supposition. The results of these calculations are shown in Tables 1 and 2, where S is the area of face C.

Comparison of the S values in Table 2 with the area per molecule as well as of a and b parameters with minimum possible distances between BEDT-TTF groups shows that a single reasonable variant is four molecules per unit cell in one monolayer, i.e. $Z=4$. Values of $Z>4$ seem to be quite

Table 2

Parameters of the unit cell in the crystalline structure of the LB film of the heptadecylcarboxymethyl-BEDT-TTF charge transfer salt

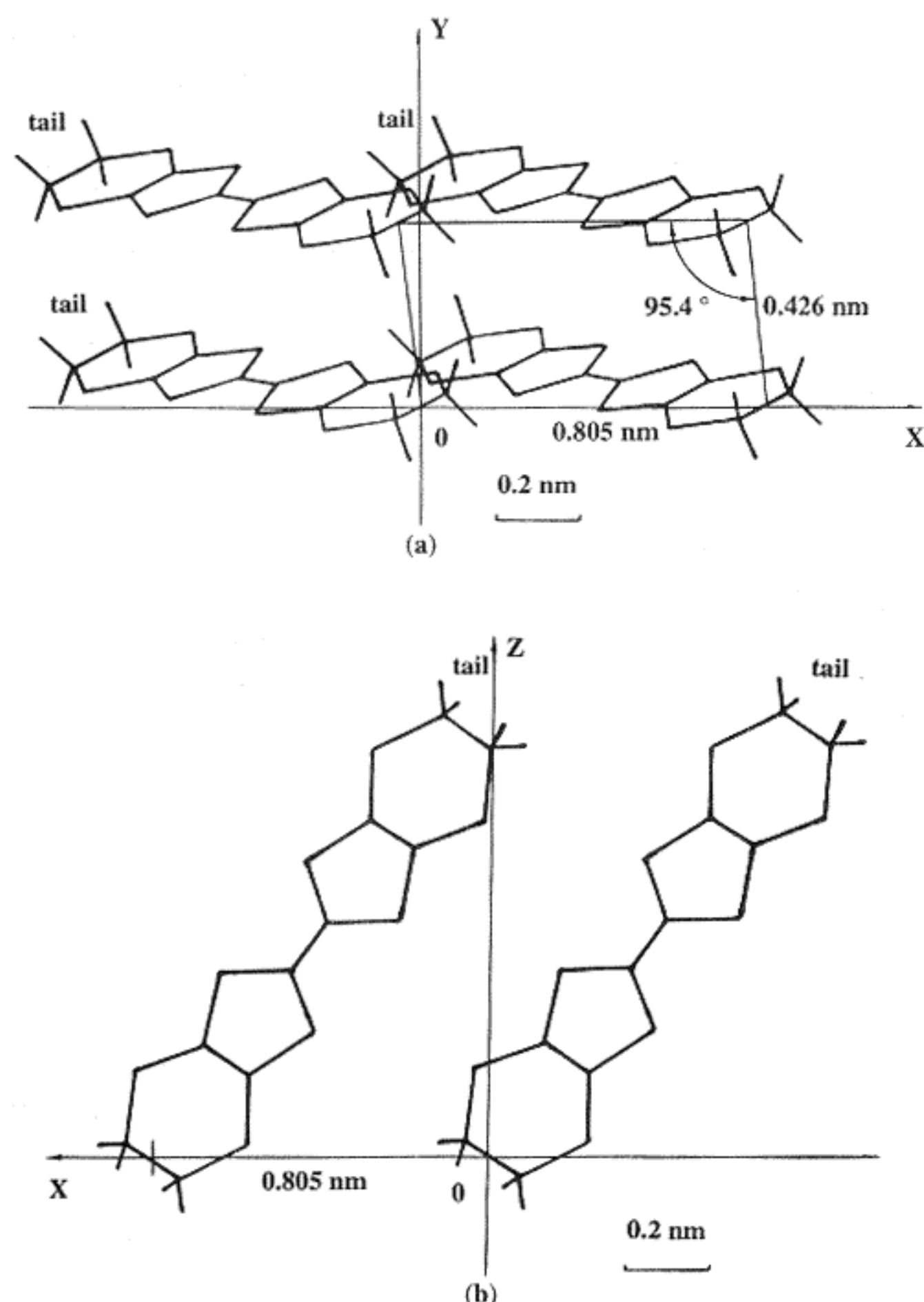| Variant of the structure	a (nm)	b (nm)	γ (°)	S (nm^2)
I	1.611	0.853	95.4	1.369
II	1.619	1.254	99.4	2.003
III	1.460	1.420	96.8	2.059

Fig. 4. Probable model of the BEDT-TTF group packing in the absence of charge density wave with projections on the XY (a) and XZ (b) coordinate planes.

unrealistic. Such an unusual Z value in one monolayer has already been determined for the films of hexadecyl-BEDT-TTF [11] and can be explained by the arising charge density wave in closely packed conducting BEDT-TTF stacks, which is normal for organic metal crystals of similar non-surfactant compounds. Possible reasons of the behaviour observed are discussed below. Under the condition of Z=4, unit cell I in Table 2 is realized. Even if we suppose spreading of the compound at the air–water interface to be unsatisfactory,
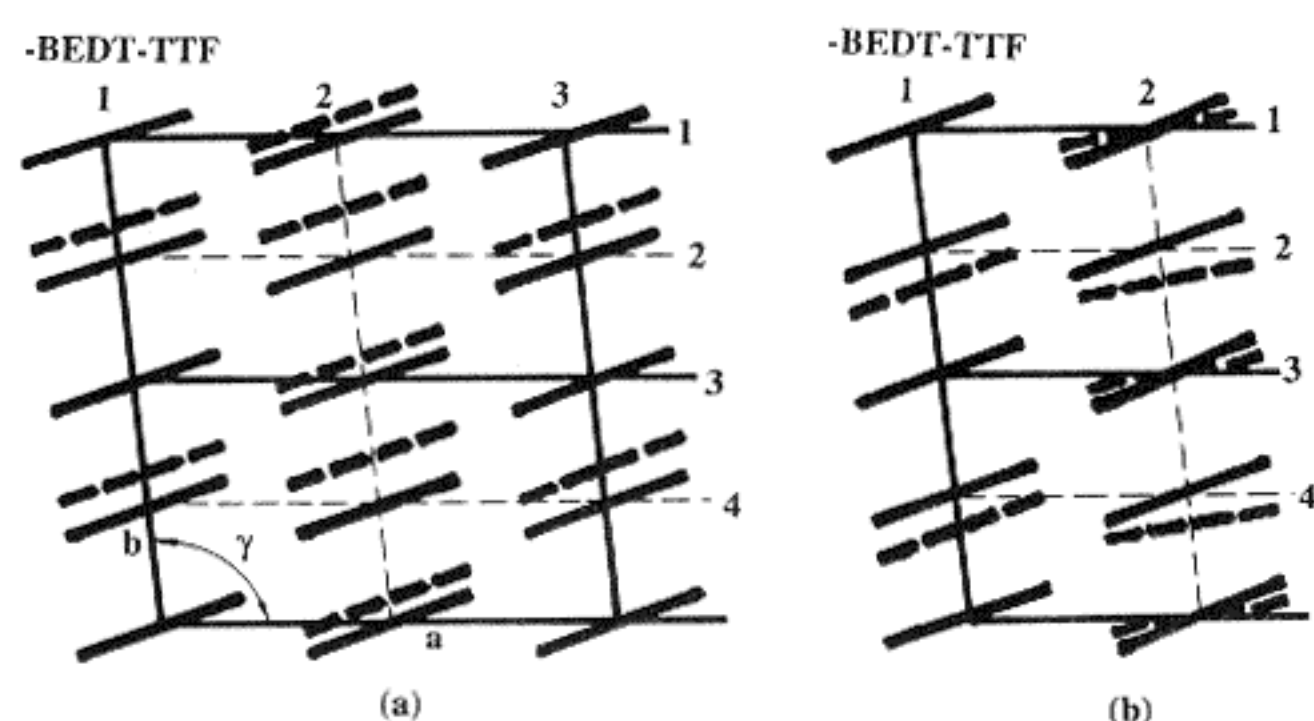

Fig. 5. Possible structure rearrangements caused by a charge density wave arising along closely packed conducting BEDT-TTF stacks for a shift (a) and turn (b) of the molecules in neighbouring rows.

which can result in the area per molecule being considerably less than the S/Z value, variants II and III are in contradiction with the presented X-ray data. Indeed, the thickness of the bilayer evaluated as before with an area per molecule of 0.50–0.51 nm^2 is equal to 3.4–4.0 nm, which is not proportional to the period value. Thus, we conclude that the parameters of the unit cell are $a = 1.611 \pm 0.031$ nm, $b = 0.854 \pm 0.011$ nm and $\gamma = 95.4 \pm 2.3°$.

To understand probable reasons of the arising structure with four molecules per unit cell in one monolayer we shall proceed first from a hypothetical unit cell with $Z = 1$, i.e., with $a' = a/2 = 0.805$ nm, $b' = b/2 = 0.427$ nm and $\gamma = 95.4°$. In principle, packing patterns of the molecules in such a unit cell can be determined with the method developed in [14]. However, in the present case these calculations are somewhat useless because the initial hypothetical unit cell is not realized, whereas for a unit cell with $Z = 4$ the method is not applicable. For this reason, we applied here only the first step of this method to the BEDT-TTF fragments without hydrophobic tails. Close packing patterns are calculated at this stage under the supposition that atoms are rigid balls with radii equal to the van der Waals radii. It appears that several solutions are possible. For discussion we choose one of them shown in Fig. 4 as the most probable because the tilt angle of the BEDT-TTF axis is the highest for this model, which results in the highest packing coefficient. Angles of group rotation around the Z, X and Y coordinate axes which are carried out successively are equal to $\varphi_Z = -23.5°$, $\varphi_X = 6.0°$ and $\varphi_Y = 37.0°$, respectively.

The angle is positive if the rotation is performed clockwise. In the initial position, the plane of the group coincides with the XZ coordinate plane. When calculating the model we neglected the fact that the BEDT-TTF group is not completely flat. Undoubtedly, exact calculations for the molecules with tails and with minimization of the energy of molecular interaction can make another model more advantageous, but also such a rough approach gives us one parameter, which can be considered as real, because it varies by several per cent only for different models determined. This is the angle between the BEDT-TTF axis and normal to the layer plane equal to $36 \pm 2°$.

In the model proposed, closely packed stacks of the BEDT-TTF fragments are arranged along the b' side of the hypothetical unit cell and these rows are quasi-one-dimensional conductors. Hence, in this direction a charge density wave may arise. Dimerization of the molecules will take place as shown schematically in Fig. 5(a) for the odd rows of the molecules resulting in doubling of this period; but exactly the same structure of even stacks will be hardly possible. It is clear, for example, that under such a supposition even molecules of the first row and odd molecules of the second row will try to penetrate into each other and strong repulsion of the latter must arise. Different rearrangements of the structure can take place to achieve the minimum of energy of molecular interaction; two of them are shown in Fig. 5. These are shifts of the even rows with respect to odd ones (a) and turns of

the molecules (b), both resulting in doubling of the period in the X direction. In reality, more complicated rearrangements appear of course, but the general principle seems to be true.

3.5. Electrical properties

Electrical conductivity after deposition assigned only to the regions of BEDT-TTF fragments usually equals 1.5–2 ohm^{-1} cm^{-1}. Additional doping with iodine may increase this value up to 4 ohm^{-1} cm^{-1}. This increase of conductivity shows that optimum degree of oxidation of the donor molecules by $FeCl_3$ is not achieved under the conditions used. Thus, we can expect some additional improvement of conductivity due to selection of the water subphase of new more complex composition. Reproducibility of the conductance value is usually better than 15% if the conditions of sample preparation are carefully controlled. The films of heptadecylcarboxymethyl-BEDT-TTF similar to those of hexadecyl-BEDT-TTF are conducting when they are deposited from the surface of pure water, probably due to some uncontrolled doping. In this case, conductivity is equal to 0.01–0.2 ohm^{-1} cm^{-1} and can change several times from one experiment to another in spite of exact repetition of technological conditions and the use of the same substrate. After doping with iodine, conductance increases five to ten times, but it is impossible to obtain a reproducible value of conductivity. Thus, we conclude that the use of $FeCl_3$ for donor oxidation is the main reason of improvement in the conductance reproducibility.

The sensitivity of the films to the electron beam effect is practically the same as that of hexadecyl-BEDT-TTF multilayers [6] and is equal approximately to 10^{-4} C cm^{-2} at an accelerating voltage of 2 kV. This value is measured when conductivity decreases 1000 times. Such a difference seems to be sufficient for isolation of two separated conducting elements when carrying out some lithographic process on the basis of conductivity destruction.

4. Conclusions

The results show that uniform highly conducting LB films can be created on the basis of heptadecylcarboxymethyl-BEDT-TTF compound without the use of donor–acceptor mixtures to improve spreading of the monolayers at the air–water interface. The films are sensitive to the electron beam effect. Conductive properties of the heptadecylcarboxymethyl-BEDT-TTF films are similar to those of hexadecyl-BEDT-TTF in spite of the large difference in their structures. For further increase of conductivity, the use of more complicated water subphase compositions is proposed in future work.

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