Observation of metallic conductivity down to 14 K in Langmuir-Blodgett films based on BEDO-TTF and behenic acid

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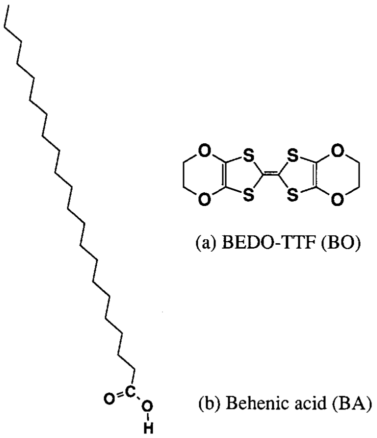
Metallic Langmuir-Blodgett (LB) films were fabricated by mixing bis-ethylenedioxy-tetrathiafulvalene, or BEDO-TTF and behenic acid. The maximum conductivity in as-deposited LB films reached 40 S/cm at room temperature. Temperature dependence of the dc conductivity shows metallic behavior down to 14 K. Percolation does not dominate conduction in these LB films. A possible layered model of the LB films is proposed from the results of surface pressure-area isotherm, infrared absorption, and x-ray diffraction experiments. [S0163-1829(97)50616-3]

The use of metallic Langmuir-Blodgett (LB) films for electronic devices is an area of significant interest.[1,2] The merit of the LB technique is characterized by the fabrication of layer-by-layer structure, which could be applied to future nanoscale device. For the realization of metallic conducting LB films, the most important point is the establishment of a two-dimensional (2D) network of electroactive parts with the overlap between molecular orbitals.[3,4] From the point of view, the classical molecule for conducting LB films, which is composed of both the long alkyl chain part and the electroactive one,[1,2] has a difficulty to form the 2D conducting network. It is because the lateral packing of such LB films is governed by the alkyl chains, and the electroactive parts are not always in the best position for making closer contact with each other.[5] To overcome the above difficulty, we developed a strategy in which alkyl chain and electroactive parts are replaced by separated molecules: a fatty acid molecule and a simple electroactive molecule, respectively.

We have examined the above idea by the mixing system of behenic acid (BA) and oxygen substituted TTF derivative such as bis-ethylenedioxy-tetrathiafulvalene, or BEDO-TTF (BO) (Ref. 6) or 4,5-ethylenedioxy-4′,5′-ethylenedithio-tetrathiafulvalene.[7,8] It was found that a mixed molecular system of BO and BA provided (see Fig. 1) highly conducting LB films without secondary treatment. The LB films have a maximum conductivity up to 40 S/cm at room temperature and metallic temperature dependence down to 14 K. The exponential decrease of conductivity originating from the percolation effect at low temperature[9] was not observed, which indicates that the highly homogeneous structure is organized in the LB films. In addition, the results of x-ray diffraction also imply the formation of an uniform Y-type structure. In conclusion, a homogeneous layered structure involving a 2D network by BO molecules is realized in the LB films giving rise to highly conducting states.



(a) BEDO-TTF (BO)

(b) Behenic acid (BA)

FIG. 1. Molecular structures of BEDO-TTF (BO) and behenic acid (BA).

For the preparation of LB films, each chloroform solution of BO (7.38×10^{-4} mol/l) and BA (8.22×10^{-4} mol/l) was prepared separately. The solutions of BO and BA were mixed under the molar concentration ratio of 2:1 (BO:BA) prior to being spread on a pure water surface. The deposition

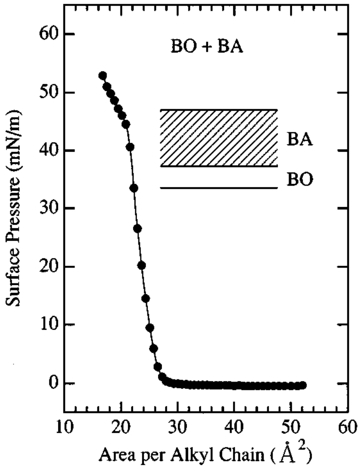


FIG. 2. Surface pressure-area (Π-A) isotherm for BO+BA mixture system at 2:1 molar ratio. The isotherm was obtained on the pure water surface at room temperature. The inset shows a possible model of molecular organization on the water surface.

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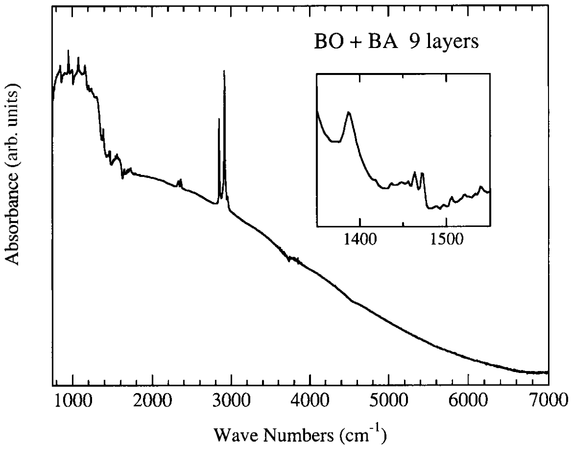

FIG. 3. Infrared absorbance spectrum for BO+BA LB films. The inset is an expanded view of the spectrum near the deformation modes of the methylene group.

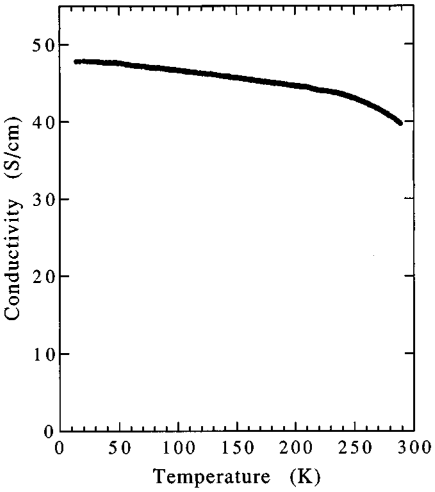

FIG. 4. Temperature dependence of the conductivity for seven layers of BO+BA LB films at 2:1 molar ratio.

of the Y-type LB films on the substrate was carried out by alternating downstroke and upstroke depositions at a surface pressure of 25 mN/m. A constant transfer ratio of 1.0±0.1 was observed in both directions. The glass and CaF_2 substrates were used for electrical conductivity and Fourier transform infrared (FTIR) absorption measurements, respectively. On the glass substrate, four gold electrodes separated with 0.3-mm gaps were made by evaporation before the deposition of the films. Measurements of electrical conductivity down to 14 K were carried out in a closed-cycle helium cryostat. The dc four-probe method was performed under 1.0 μA current flow. FTIR spectra were recorded in the N_2 atmosphere with Nicolet Magna 550 spectrometer. We also performed x-ray-diffraction experiments in 2θ-θ scan mode using a Rigaku RAD-IIA diffractometer after the FTIR measurements.

Figure 2 exhibits the surface pressure-area (Π-A) isotherm of the BO+BA system. The horizontal axis shows the observed area per molecule of BA. In the isotherm, the area at a surface pressure of 30 mN/m was 22 Å^2, which is quite close to the value of a pure BA monolayer on a water surface (20 Å^2 at 30 mN/m).[10] Also, the profiles of the isotherm did not change even when the BO concentration was decreased to 1:1. These behaviors indicate that the lateral packing of the present system is determined by BA only. A possible structural model consistent with the observed Π-A isotherms is shown on Fig. 2. In the model, a bilayer structure is formed on the water surface: the upper layer is made of BA, which brings about the lateral packing of this system, and the lower layer is made of BO, which does not have much hydrophobic character. We consider that this bilayer formation on the water surface could be a key in realizing a uniform 2D network of BO molecules in the LB films, which will be discussed later.

Figure 3 shows a representative FTIR spectrum for nine layers of as-deposited BO+BA LB films. The most significant feature of the spectrum is existence of the following two structures: a broad charge-transfer band appearing over the spectrum region with its peak around 1600 cm^{-1} and a series of vibronic mode bands existing in the region from 800 to 1300 cm^{-1}. These bands are characteristic of the formation of the mixed valence dimer states of BO molecules, which is consistent with the high conductivity of the films. The BO molecule requires a counter anion to form the mixed valence dimer, so that the anion must exist in the LB films. However, it is not clear what kind of molecule plays the role of anion. This point is an open question at the present stage. Structural information is also obtained from the FTIR spectrum. There are two sharp absorption peaks assigned as deformation modes of methylene group (δCH_2) at 1464 and 1473 cm^{-1}. The presence of the doublet peaks indicates that the symmetry of the subcell composed of alkyl chains of BA is orthorhombic.[11] In Table I, the observed absorption frequencies on several vibrational modes are shown together

TABLE I. Observed frequencies of vibrational modes in several compounds of BO.

	Frequencies of vibrational modes				
	B_{2u} (48) (cm^{-1})	Ag (7) (cm^{-1})	B_{2u} (50) (cm^{-1})	Ag (8) (cm^{-1})	charge of BO (e)
BO neutral (Ref. 12)	1082	1011	963	864	0
$BO_3Cu_2(NCS)_3$ (Ref. 12)	1082	1007	960	862	+0.33
BO+BA (LB)	1078	1001	955	853	
$BO_2ReO_4H_2O$ (Ref. 12)	1077	1001	955	855	+0.5

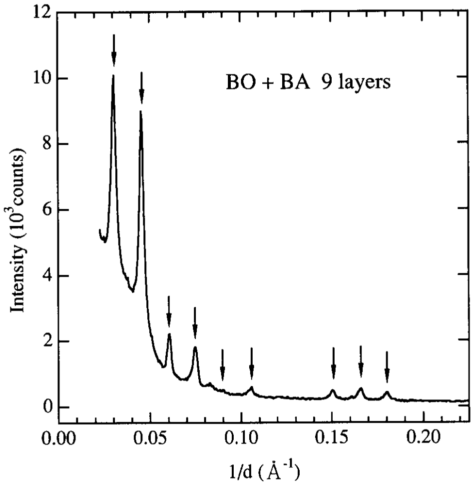

FIG. 5. X-ray diffraction profile for nine layers of BO+BA LB films.

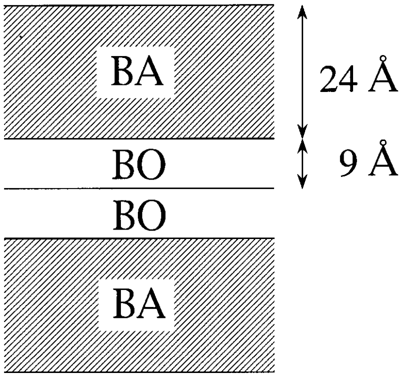

FIG. 6. A possible layered model of BO+BA LB films.

with those of neutral BO,[12] $BO_2ReO_4 \cdot H_2O$,[12] and $BO_3Cu_2(NCS)_3$.[12] From the frequency shift from the neutral BO, the estimation of the degree of average charge transfer ρ is possible.[12] It is clear that each value of the frequency shift of the vibrational modes on the LB films is very close to that on $BO_2ReO_4 \cdot H_2O$ ($\rho = +0.5$), which indicates that ρ of BO in the LB films is $+0.5$.

Figure 4 exhibits the temperature dependence of the conductivity for the LB films of seven layers that was measured with increasing temperature from 14 K. The conductivity was calculated by using the sample thickness estimated from the stacking periodicity observed by x-ray diffraction. In Fig. 4, a metallic conductance showing a negative temperature derivative was observed in the whole temperature range. Previously reported conducting LB films revealed an exponential decrease of the conductivity due to existence of insulating domains even if their intrinsic properties are metallic.[9] We did not observe such a decrease of the conductivity, which indicates that there is no effective insulating domains in this LB films.

Figure 5 shows an x-ray diffraction profile for the LB films of nine layers, where $1/d \equiv (2 \sin \theta)/\lambda$ (λ is the wavelength). Since LB films have a layered structure with a periodicity d_0, the $00l$ diffraction peaks appear at the positions of l/d_0 ($l = 1,2,3,\ldots$). With $d_0 = 66$ Å, one would expect the peaks at $1/d = 0.015, 0.03, 0.045, \ldots$, most of which are present on the figure (indicated by arrows). The origin of the periodicity is attributed to BO+BA layered stacking. The profiles of BO+BA peaks were sharp and strong even for nine layers, which implies that a highly homogeneous layered structure of BO+BA is constructed in the LB films. In the diffraction profile, there is no major periodic peaks except the peaks of the BO+BA layer. From the above consideration, it is concluded that the BO+BA system realizes a LB film built by a single stacking periodicity.

Figure 6 shows a possible layered model of the LB films on the basis of the obtained results. The model is based on the *Y*-type structure built of the bilayer film on the water surface (Fig. 2): two conducting BO layers are located between the insulating BA layers. The results of FTIR experiments show that the BA layer has orthorhombic subcell. The two types of orthorhombic subcell are known for BA layer: *B* form (53 Å) and *C* form (48 Å).[13] Taking account of the thickness of the BO layer, the latter form is more probable. Then, the thickness of one BA layer would be 24 Å, which is half of the *C*-form layer thickness, and it would be 9 Å for one BO layer, accordingly.

The high conductivity and metallic behavior of temperature dependence of this system should be closely related to its film structure. In the model of Fig. 6, it is possible for the BO molecules to make closer contact to form a 2D conducting network that provides a stable metallic state at low temperatures. In addition, the absence of insulating domains stabilizes a metallic behavior in macroscopic range. If not, the conductivity decreases exponentially at low temperature because of the possible percolation effect that is brought about by the existence of insulating domains.[9] For example, metallic LB films of BO-C_{10} tetracyanoquinodimethane (TCNQ) (Ref. 14) and BO_2-$(MeO)_2$ TCNQ (Ref. 15) are known to show the exponential decrease of the conductivities below 250 and 180 K, respectively. Therefore, we consider that two structural features, the existence of a 2D conducting network and the absence of the insulating domains, are quite important for the realization of metallic conducting LB films. In our case, the formation of the optimized structure by the BO+BA system probably originates from satisfying the two conditions above. First, the BO molecules tend to make C-H···O contacts[16] which would lead the formation of a 2D network by the donor molecules. Second, the bilayer formation on the water surface provides the LB films with a uniform layered structure, which prevents the appearance of insulating BA domains.

Finally, the question remains as to what kind of molecule plays the role of anion. Oxygen in air or BA molecule could be a candidate. To clarify this point, further investigation of those LB films is required.

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