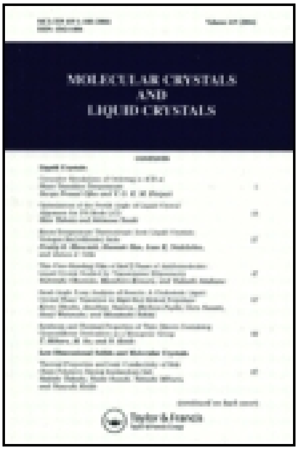

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Langmuir-Blodgett Films of Bedo-TTF / Behenic Acid : Effect of the Molecular Fraction of Bedo-TTF and of the Substitution of Behenic Acid for other Amphiphilic Molecules

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LANGMUIR-BLODGETT FILMS OF BEDO-TTF / BEHENIC ACID : EFFECT OF THE MOLECULAR FRACTION OF BEDO-TTF AND OF THE SUBSTITUTION OF BEHENIC ACID FOR OTHER AMPHIPHILIC MOLECULES

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Abstract : We report the conducting properties of Langmuir-Blodgett films obtained by mixing BEDO-TTF with various molecules. Conductivity was observed when BEDO-TTF was mixed with fatty acids and a phosphate. On the other hand, the association of BEDO-TTF and docosanol led to insulating properties. This suggests that the polar head group of the amphiphilic molecules contributes to the partial charge-transfer process of BEDO-TTF.

Keywords : Langmuir-Blodgett films, organic conductors, tetrathiafulvalene (TTF) derivatives

INTRODUCTION

Studies on charge-transfer salts have mainly concentrated on single crystals. However, their mechanical fragility and the difficulty to obtain large crystals have restricted the prospects for practical applications. Besides, thin-filmed charge-transfer salts are promising materials providing a great variety of potential applications in molecular electronics and photoelectronics [1].

The Langmuir-Blodgett (LB) technique allows the organization of a molecular film at the air/water interface and subsequently enables the formation of multilayered films by raising and lowering a substrate through the interface. This way, both surface dimension and film thickness can be controlled.

Various strategies have been explored for obtaining metallic conductivity in LB films : formation of a neutral TTF derivative with long alkyl chain, followed by chemical oxidation [2], preparation of the amphiphilic charge-transfer complex in solution as a starting material to fabricate LB films [3] , etc. Some of these LB films successfully exhibited metallic conductivity at room temperature but they showed semiconducting properties at low temperatures.

We have developed a new strategy in order to achieve well-defined metallic films down to liquid helium temperature (at least down to 14 K) [4,5]. The starting molecules are an oxygen-substituted-tetrathiafulvalene, BEDO-TTF and a fatty acid, behenic acid (Figure 1). Metallic conductivity was obtained without any further secondary treatment.

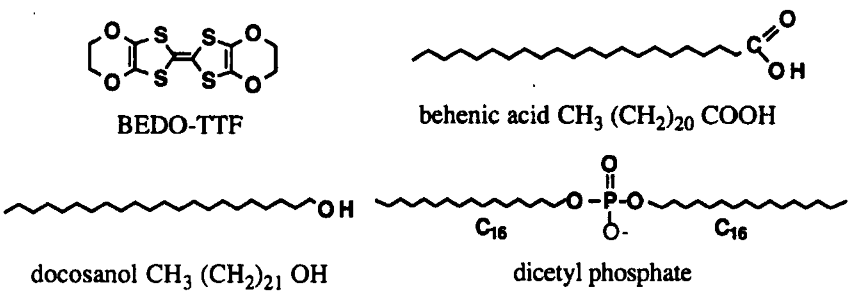

FIGURE 1 Molecular structures of BEDO-TTF, behenic acid, docosanol and dicetyl phosphate.

This paper is a part of the study to clarify the charge-transfer mechanism in these films. We report the conducting properties observed by FTIR spectroscopy and dc conductivity for various compositions of BEDO-TTF and behenic acid, and subsequently discuss the effect of the substitution of behenic acid for other amphiphilic molecules : stearic acid, docosanol and dicetyl phosphate (see Figure 1 for chemical structures).

EXPERIMENTAL

BEDO-TTF was synthesized as shown in reference [6]. Behenic and stearic acids were purchased from Fluka, dicetyl phosphate (also called dihexadecyl phosphate) from Sigma. A monolayer was prepared on the water surface by spreading a chloroform solution of the mixture of BEDO-TTF and the amphiphilic molecule (fatty acid, fatty alcohol or phosphate). The resulting monolayer was transferred onto the surface of a substrate by alternating downstroke and upstroke depositions under a constant surface pressure, 20 mN/m. The transfer ratios were close to unity except in the case of BEDO-TTF / docosanol for which 7 layers of behenic acid needed to be pre-deposited on the substrate prior to the film deposition in order to obtain a good transfer ratio. A calcium fluoride (CaF_2) plate was used as a substrate for IR measurements. A glass plate on which four gold electrodes separated with 0.3 mm gaps was prepared in order to measure electrical conductivity.

RESULTS AND DISCUSSION

BEDO-TTF / fatty acid

We have already reported the formation of a stable and highly conducting Langmuir-Blodgett film from the association of BEDO-TTF and behenic acid [4,5]. The dc conductivity of this film was 40 S/cm at room temperature, and increased with decreasing temperature down to at least 14 K, which is characteristic of metallic conductivity. The FTIR absorption spectra of an LB film of BEDO-TTF / behenic acid in the ratio 1/1 or 2/1 are shown in Figure 2. A broad electronic absorption band centered around 1600 cm^{-1}, together with a series of vibronic mode bands are observed. These absorption bands are characteristic of the formation of a mixed-valence state of BEDO-TTF molecules. The creation of the mixed valency of BEDO-TTF requires the presence of a counter-ion. In order to identify this species, the ratio of BEDO-TTF to behenic acid was varied between 0/1 and 2/1 and FTIR spectroscopy was performed (Figure 2).

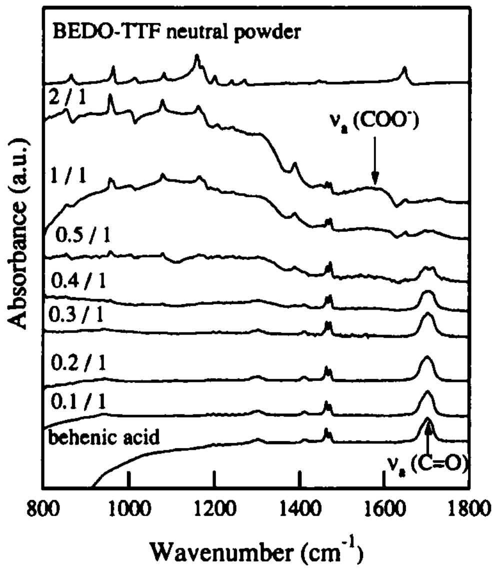

FIGURE 2 FTIR spectra of BEDO-TTF neutral powder, behenic acid and LB films of BEDO-TTF / behenic acid of various molecular ratios.

As the molar fraction of BEDO-TTF increased, the absorption band at 1708 cm^{-1}, assigned to ν_a (C=O), decreased and a band centered around 1570 cm^{-1} appeared. We assigned this band to ν_a (COO$^-$). This phenomenon is linked to the increase in the intensity of the electronic absorption band and of the vibronic ones characteristic of electronic conductivity. Therefore, the increase in the conductivity is accompanied with the formation of the COO$^-$ ion, which could play the role of the counter-ion necessary to create the mixed-valency of BEDO-TTF. In order to confirm this hypothesis we exchanged behenic acid for other amphiphilic molecules : fatty acids, docosanol and dicetyl phosphate.

By using other fatty acids we tried to verify that keeping the same polar head group but changing the length of the alkyl chain had no effect on the appearance of conductivity in the LB films. When stearic acid $CH_3(CH_2)_{16}COOH$ was mixed with BEDO-TTF, the FTIR spectra were similar to those obtained with behenic acid, i.e. a broad electronic absorption band and vibronic bands appeared (see Figure 3). The conductivity reached

60 S/cm at room temperature, which is higher than with behenic acid.

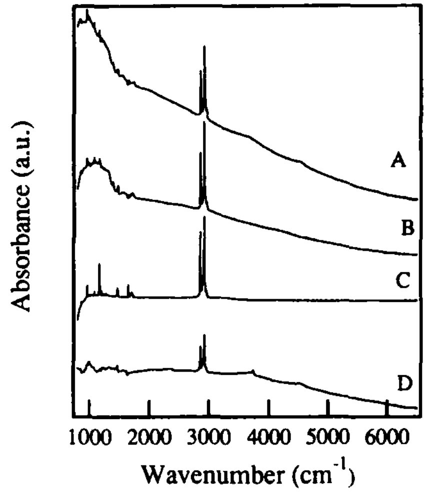

FIGURE 3 FTIR spectra of LB films of BEDO-TTF mixed with A: stearic acid; B: behenic acid; C: docosanol; D: dicetyl phosphate in the molecular ratio 1/1.

BEDO-TTF / docosanol

BEDO-TTF was mixed with a fatty alcohol (docosanol) in order to find out if a mixed-valence state could be observed with a molecule which is not subject to dissociation. The FTIR spectrum of the BEDO-TTF / docosanol LB film is shown in Figure 3. Neither broad electronic absorption band nor vibronic bands could be observed. Therefore, when BEDO-TTF was mixed with docosanol, no mixed valence state was formed. The same results were obtained when BEDO-TTF was mixed with octadecanol. Hence, the ability of the amphiphilic molecule to dissociate might play an important role in the observation of the conductivity.

BEDO-TTF / dicetyl phosphate

We tried to make LB films by mixing BEDO-TTF with a amphiphilic ion dicetyl phosphate. The FTIR spectrum obtained from BEDO-TTF / dicetyl phosphate is shown in Figure 3. A broad electronic absorption band was observed. This band was centered around 3000 cm^{-1}, which is much higher than that in the case of BEDO-TTF / fatty acid. This suggests that the conductivity is relatively lower [7]. This was confirmed by the electrical conductivity measurements which indicated a conductivity of 0.05 S/cm at room temperature.

CONCLUSION

The mixture of BEDO-TTF with behenic acid results in a metallic LB film down to at least 14 K without any secondary treatment. The origin of the counter-ion necessary to create a mixed-valence state in BEDO-TTF was investigated by varying the ratio of BEDO-TTF to behenic acid and by substituting behenic acid for other amphiphilic molecules. A mixed-valence state was only observed when BEDO-TTF was mixed with a fatty acid or dicetyl phosphate. In the case of docosanol, the LB films were insulating. The present results suggest that the counter-ion comes from the ionization of the polar head group of the amphiphilic molecule mixed with BEDO-TTF in order to form metallic LB films. This will be submitted to further investigations on the charge-transfer process between BEDO-TTF and the polar head group on the water surface.

REFERENCES

1 M. R. Bryce, M. Petty, Nature, **374**, 771 (1995)
2 C. Dourthe, M. Izumi, C. Garrigou-Lagrange, T. Buffeteau, B. Desbat and P. Delhaes, J. Phys. Chem., **96**, 2812 (1992)
3 T. Nakamura, Handbook of Organic Conductive Molecules and Polymers, H.S. Nalwa Ed., Wiley & Sons (1997)
4 H. Ohnuki, T. Noda, M. Izumi, T. Imakubo, R. Kato, Physical Review B, **55**, R10225 (1997)
5 H. Ohnuki, T. Noda, M. Izumi, T. Imakubo, R. Kato, Supramolecular Science, **4**, 413 (1997)
6 T. Suzuki, H. Yamochi, H. Isotalo, C. Fite, H. Kasmai, K. Liou, G. Srdanov, F. Wudl, P. Coppens, K. Maly and A. Frost-Jensen, Synthetic Metals, **41-43**, 2225 (1991)
7 P. Delhaes, Lower-Dimensional Systems and Molecular Electronics, R.M. Metzger *et al.* Ed., Plenum Press, New York (1991)