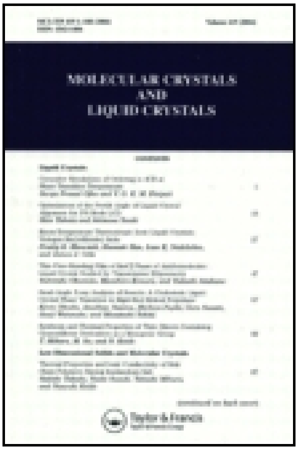

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Takayoshi Nakamura , Hiroaki Tachibana , Motoo Wmura , Yasuhiro Miura , Mutsuyoshi Matsumoto , Motoo Tanaka , Reiko Azumi , Eiichiro Manda & Yasujiro Kawabata (1992): Molecular Systems of Photoactive and Conductive LB Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 218:1, 147-152

To link to this article: http://dx.doi.org/10.1080/10587259208047031

Mol. Cryst. Liq. Cryst. 1992, Vol. 218, pp. 147–152
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Printed in the United States of America

MOLECULAR SYSTEMS OF PHOTOACTIVE AND CONDUCTIVE LB FILMS

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Abstract Photoactive and conductive Langmuir–Blodgett films are described utilizing cyclodextrin derivatives, TCNQ radical salts, metal–dmit complexes and fullerenes to form 0, 1, 2, and 3–dimensional molecular systems.

INTRODUCTION

Langmuir–Blodgett (LB) technique is one of the most powerful tools for the construction of organic thin films in which the molecules are assembled properly. Molecular systems of various functions would be realized by LB method, aligning specific molecules at specific positions to interact each other. The LB system itself should be 2–dimensional system due to the small thickness of the film. However, we can introduce molecular assemblies with various dimensionality in this system to form novel kinds of the molecular systems. In this paper, we will report four kinds of functional LB films which form 0, 1, 2, and 3–dimensional molecular systems.

0–DIMENSIONAL SYSTEM

The cyclodextrin (CD) molecules have a cavity in which guest molecules or ions can be included forming inclusion compounds. The molecules in the cavity should be in ordered state regulated through the electrostatic or Van der Waals interaction between the substituent groups of the sugars and the included molecule.

We introduced long alkyl chains into β–CD through the amino group (Figure 1). This molecule formed a stable monolayer at the air–water interface and transferred to solid substrates.[1] The azobenzene derivatives were included in the LB films by following two methods. 1) An azobenzene derivative and the CD was dissolved in a chloroform solution which was spread on a water. 2) The CD solution was spread on a water containing a water–soluble azobenzene derivative.

The azobenzene derivatives thus included showed cis–trans photoisomerization due to the free volume in the cavity:[2] the photoisomerization of azobenzenes from small trans–isomer to relatively bulky cis–isomer is usually prohibited in solids due to the Van der Waals repulsion between neighboring molecules. This cavity also provides an isolated space from neighboring molecule forming a 0–dimensional molecular system of the included molecules.

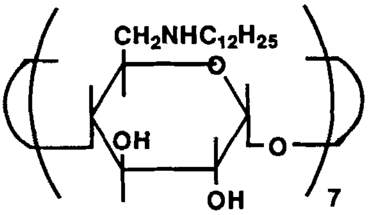

FIGURE 1. Chemical structure of the alkylated CD.

1-DIMENSIONAL SYSTEM

The 1–dimensional organic semiconductors, TCNQ anion salts, were used to construct a photochemical switching systems of the LB films. We designed an amphiphilic molecule in which three functional parts are involved: the signal from the switching unit triggered by an external stimulus is transferred through a transmission unit to change the structure and functions of a working unit (Figure 2). In this study, an azobenzene and a pyridinium–TCNQ anion salt were used as a switching and working unit, respectively.[3-4] The alkyl chain connecting two units was used as a transmission unit. In this arrangement, the cis–trans photoisomerization of the azobenzene by an irradiation of light induces the change in the structure of the 1–dimensional molecular assembly of TCNQ. Consequently, the reversible change in the lateral conductivity of the LB film is controlled by the external stimuli of the light.

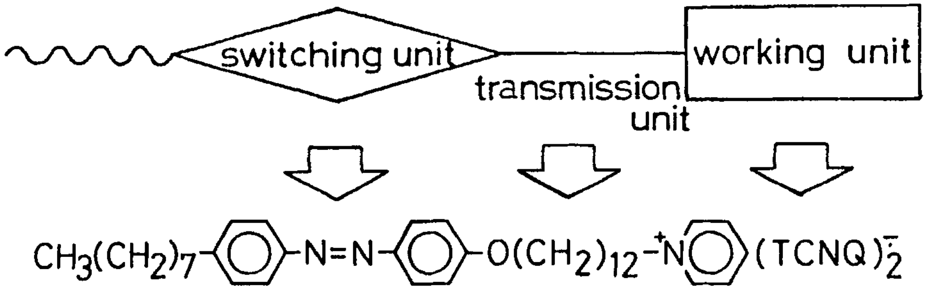

FIGURE 2. TCNQ radical salt used for the photochemical switching LB film.

Figure 3 shows the changes in the absorbance at 356 nm (the absorption due to the trans-azobenzene) and the lateral conductivity of the LB film upon alternate irradiation of UV and visible light. The reversible change in the conductivity corresponds to the cis-trans isomerization was observed, which can be repeated more than hundred times.

This system utilizes a instability of the conductivity of the TCNQ anion salts which is sensitive to the orientation of the TCNQ in the one-dimensional stacks. The orientational changes of TCNQ caused by the isomerization of azobenzene should bring the system to a metastable state and back to the initial state, forming a bistable switching system.

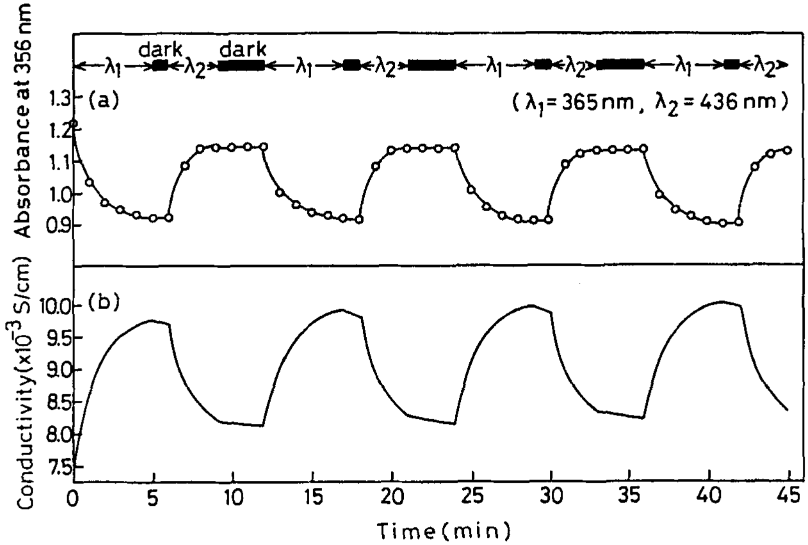

FIGURE 3. Absorbance and conductivity changes of the LB film upon alternate irradiation of UV and visible light.

2-DIMENSIONAL SYSTEM

The LB films of organic conductors with higher dimensionality were also studied in order to construct a 2-dimensional molecular system of LB films. By introducing higher dimensionality in the conductive LB system, the instability (such as Peierls instability) will be reduced and the higher conductivity will be realized.

We have chosen metal-dmit complexes as film forming materials for contracting conductive LB films more than one-dimension. The ammonium cations with long alkyl chains were used as counter cations, and Ni, Au, Pd, and Pt were used as central metal cations.[5]

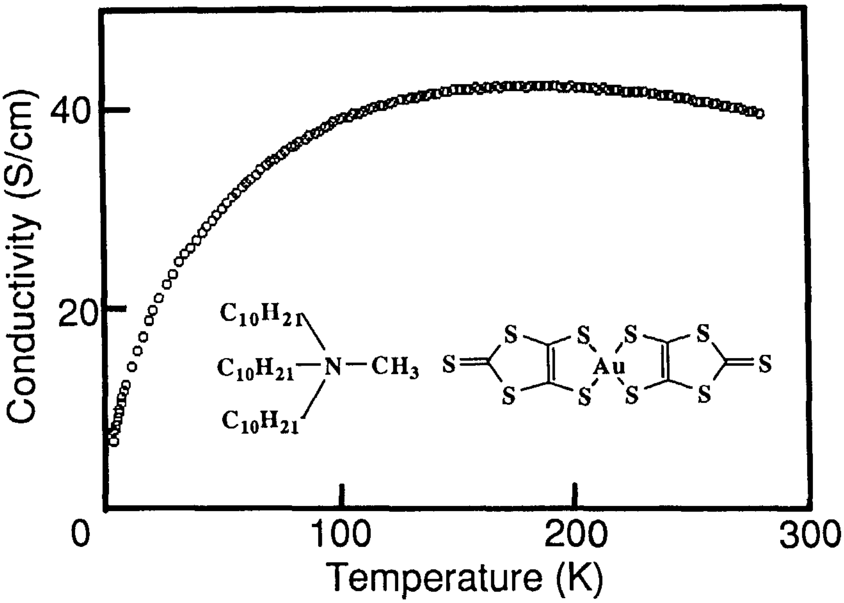

FIGURE 4. Temperature dependent conductivity for the gold-dmit LB film.

Among others, the LB films of a gold-dmit complex show a high conductivity at room temperature.[5-6] Moreover, the metallic temperature dependence of conductivity was observed down to around 200 K (Figure 4). Below this temperature the curve followed the two-dimensional variable range hopping (VRH) theory. From the measurements of thermoelectric power, the film consisted of metallic domains which were connected by less conductive regions of VRH regime.[7]

The metallic conductivity, observed in the LB films for the first time, probably comes from two-dimensional nature of the complex: the effect of the defects and disorders introduced during the film forming process will be small on the conductivity compared to that of one-dimensional conductors due to the close contact of the molecule with neighboring molecules more than one direction.

3-DIMENSIONAL SYSTEM

Fullerenes have a highly symmetric structure and unique optical, electrical, and magnetic properties such as superconductivity on doping. Various functional systems of LB films utilizing peculiar properties arising from 3-dimensional nature of the fullerenes will be realized by the construction of mixed and/or interleaved LB films of fullerenes with other functional molecules.

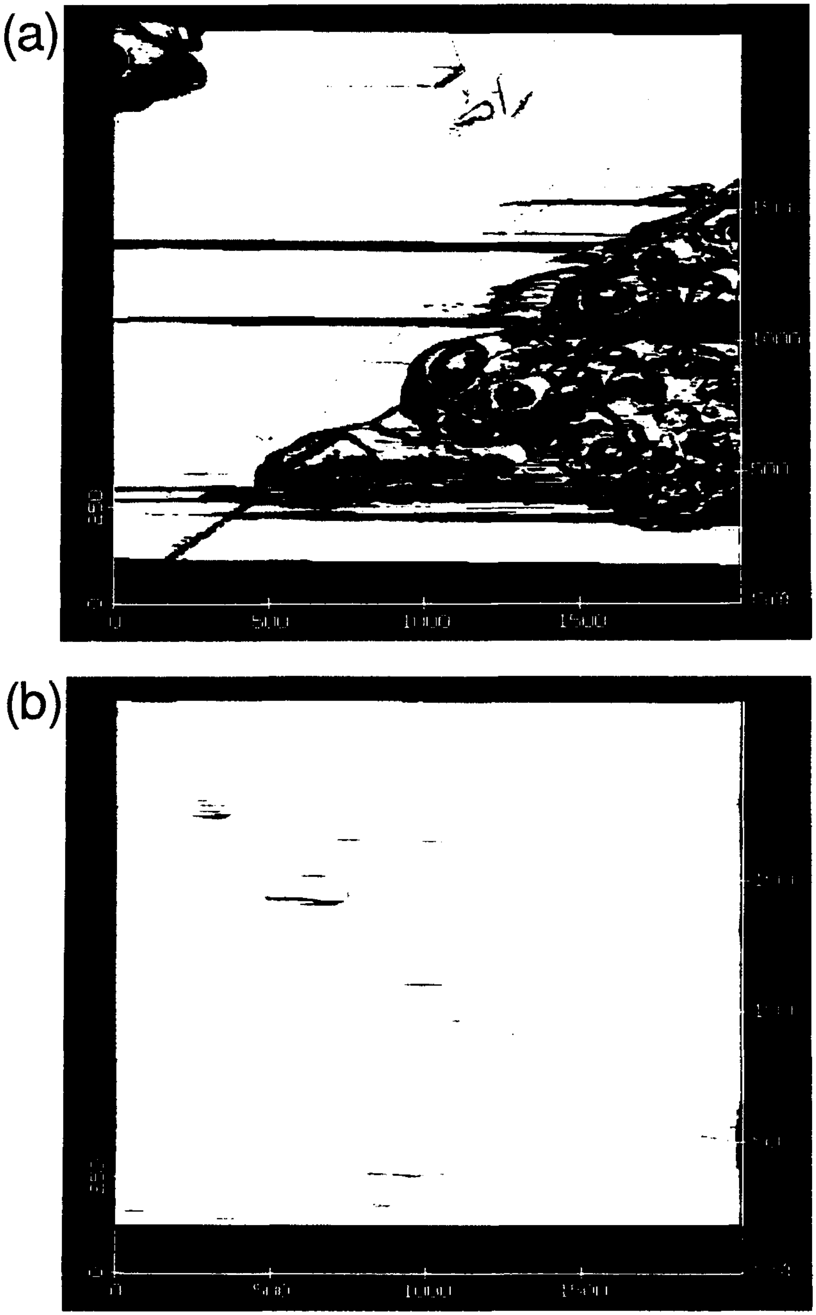

FIGURE 5. The AFM image of pure C_{60} LB film (a) and 1:1 mixed LB film of C_{60} and icosanoic acid (b).

We constructed LB films of C_{60} with and without icosanoic acid.[8] The floating layers at the air–water interface was transferred onto solid substrates by the horizontal lifting method. The surface of the film was wet in case of pure form due to the disorders present in the film. On the other hand, 1:1 mixture with icosanoic acid gave a dry surface of resultant LB film. The absorption spectra of the latter film were in good agreement with those of evaporated films. The atomic force microscope (AFM) image was obtained for the 1-layered films on the HOPG substrates. The 1:1 mixed film exhibited a flat surface as seen in Figure 5b compared with that of pure C_{60} Film (Figure 5a).

The mixed LB films of C_{60} with long-alkyl ammonium salts were also developed, which can be reduced chemically or electrochemically providing LB films of anion radicals of C_{60}.

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