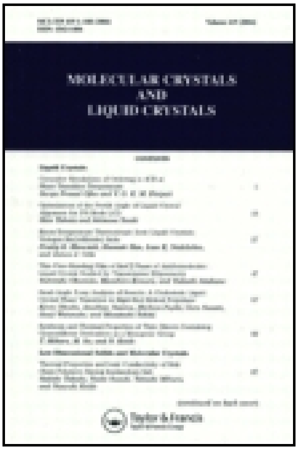

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Observation of Monolayers of a Long-chain Alkyl Dihydrophenazine Derivative for a Photoelectric Molecular Device by Atomic Force Microscopy

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Observation of Monolayers of a Long-chain Alkyl Dihydrophenazine Derivative for a Photoelectric Molecular Device by Atomic Force Microscopy

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We constructed high-quality monolayer Langmuir-Blodgett (LB) films using a novel molecule $C_{37}H_{50}N_4O_4$ synthesized by us. This molecule is the long-chain alkyl derivative which has dinitrobenzene moiety (acceptor unit) and dihydrophenazine one (donor unit) bridged by methylene group with constant distance and bond angle to behave as unimolecular photoelectric device with the control of the potential between donor and acceptor subunits. We transferred the monolayer film onto a mica plate and succeeded in getting molecular images by atomic force micoscopy.

Keywords: monolayer, molecular device, AFM, dihydrophenazine derivative

INTRODUCTION

Many studies on the molecular electronic device have been reported since Aviram and Ratner[1] suggested the construction of unimolecular organic rectifier which consisted of an electron donor subunit and an electron acceptor one, seperated by a methylene tunneling bridge. However, they were carried out mostly on the electron donor and acceptor subunit systems such as Langmuir-Blodgett (LB) films[2] which interact with each other without care about the angle as well as the distance between them.

It is very difficult to get really high-quality monolayer LB film without any structural defects and to obtain a signal exclusively from unimolecular rectifier. So in spite of these efforts it has been an open question whether these films behave as unimolecule device or not.

Photoelectronic molecular devices must induce an effective charge seperation and prevent the recombination. So it is important to consider the potential between donor and acceptor units for the selection of each units.

Recently, we have proposed the control of potential between donor and acceptor units by choosing their distance and bond angle and synthesized the compound MDNDP which have dinitrobenzene moiety (acceptor unit) and dihydrophenazine one (donor one) bridged by a methylene group with constant distance and bond angle (Fig. 1(a))[3]. Monolayer of this molecule is especially required to get singnal directly from unimolecular rectifier. Therefore we synthesized a novel long-chain alkyl derivatives $C_{37}H_{50}N_4O_4$(PNX) (Fig. 1 (b), (c)) and constructed monolayer film by the LB method. X-ray diffraction analysis showed good crystallinity of MDNDP[4]. We might expect to obtain a crystalline monolayer of PNX by this.

It has been reported that LB films usually exhibit a complex structure[5]. Thus, it is very important to construct very smooth monolayer and to observe the molecular arrangement. We constructed the monolayer in dark and clean room (class 1000) to prevent contamination from air and damage by light. From AFM measurement we can get molecular arrangement. Compared with STM, AFM is advantageous for such observation because it is not influenced by the electronic state of monolayer and effective to govern molecular structure.

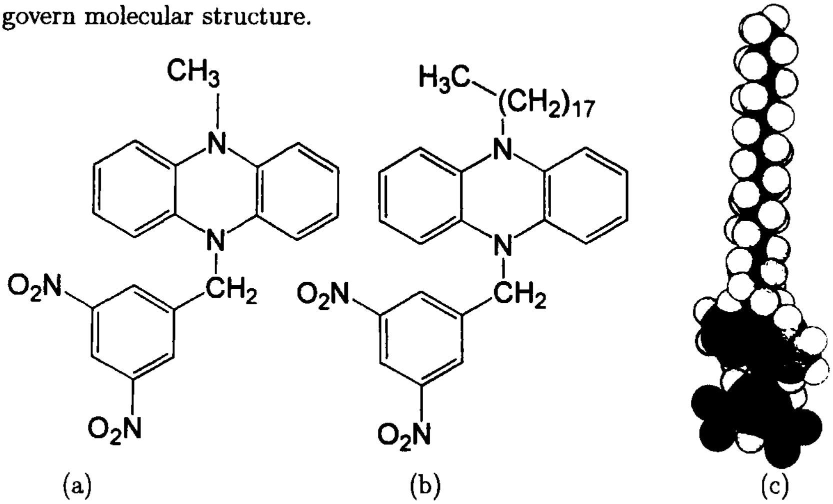

FIGURE 1 Chemical structures of MDNDP(a)[3] and PNX(b). Chemical model of PNX(c).

EXPERIMENTAL

We used a commercial Langmuir Blodgett trough (KSV Instruments KSV-5000) in clean room(class 1000) for measurement of π-A isotherm and construction of monolayer films. A solvent for spreading solution was spectrograde benzene (Dojin Chemicals). The concentration of the solution was 0.6-0.7 mg/ml. Subphase was ultrapure water and pHs were adjusted by the addition of KOH and H_2SO_4. Monolayers were spread with a gas-tight microsyringe [6], which was connected to a synchronous motor-driven micrometer, to get accurate quantity of spreading solution. Compression was carried out under constant strain rate 30 min after spreading for complete evaporation of benzene from monolayer system. We pay specially attention to constant strain compression which Kato *et. al.*[6] have proposed. Substrate was located about 1.5 mm in depth parallel to subphase surface before spreading. Film transfer was carried out by subphase-Lowering Technique[7] not to apply any stress to the monolayer while it was transferred onto a substrate. We tried to transfer by vertical dipping method, but could not get good monolayer films enough for the AFM measurements. Freshly cleaved mica was used as a substrate. The AFM observation was performed with a Nanoscope E (Degital Instruments) and PicoSPM (Molecular Imaging) at an ambient temperature in air. A silicon nitride chip on cantilever with spring constant of 0.06 N/m was used for contact AFM. The best molecular resolution was achieved in the "deflection" mode. Scan rate was 10 Hz. Typical force applied was 3×10^{-9}N.

RESULTS AND DISCUSSION

In Fig. 2 we show the pH dependence of π-A isotherm of PNX monolayers. Monolayers were compressed under constant strain rate of 10 %/min (time of observation t_{ob}=600 sec). With increasing pH of subphase, the collapse point at *a* and the peak at *b* occurred clearer. Under lower pH conditions, protonation might occurred at a nitrogen atom of dihydrophenazine group. This should induce an ionic repulsion among the monolayer molecules to prevent a formation of highly condensed two-dimensional crystalline film. The monolayer was transferred at 33mN/m with each pHs by subphase-lowering technique[7]. Beacause the monolayer of this molecule is fragile, vertical dipping method was not adequate to obtain the high-quality LB film. We could not get the molecular image of for pHs 6 and 8. The monolayer which transferred at pH 10 gave a film without any structural defects on the atomic force micoscopic scale. Fig. 3 shows the AFM molecular image of 10 nm scan of the PNX's monolayer film. All AFM images were raw data without any filtering. Fig. 4 is two-dimensional Fourier transform spectrum of Fig. 3. It clearly shows hexagonal array of molecules. Fig. 5 shows the top image of 20 nm scan of PNX monolayer. Fig. 6 is two-dimensional Fourier transform spectrum of Fig. 5. They also shows a clear molecular structrue over a wide area.

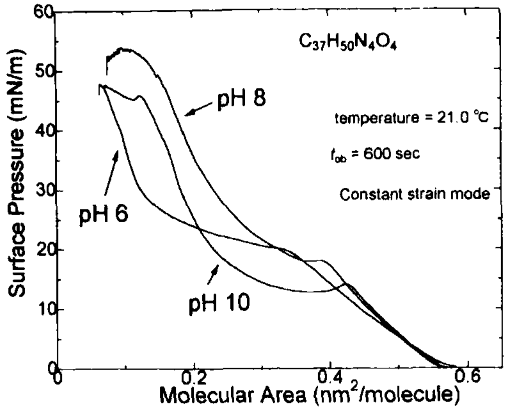

FIGURE 2 The pH dependence of π-A isotherm of PNX monolayers.

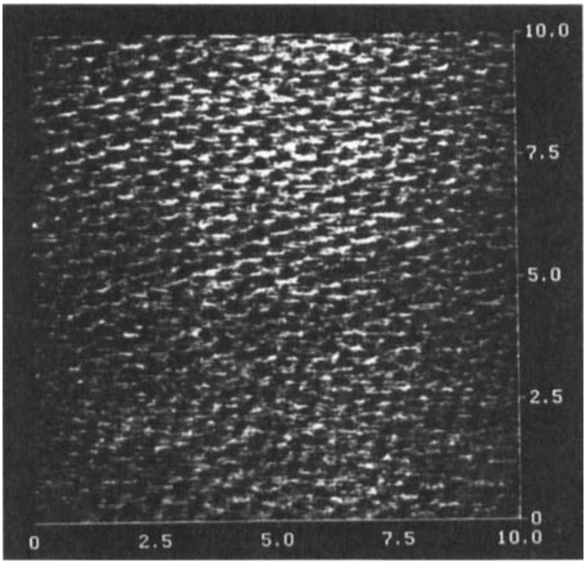

FIGURE 3 Contact AFM image of 10 nm scan.

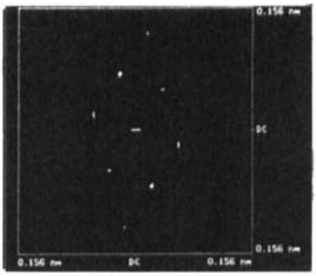

FIGURE 4 2D-FT spectrum of Fig. 3.

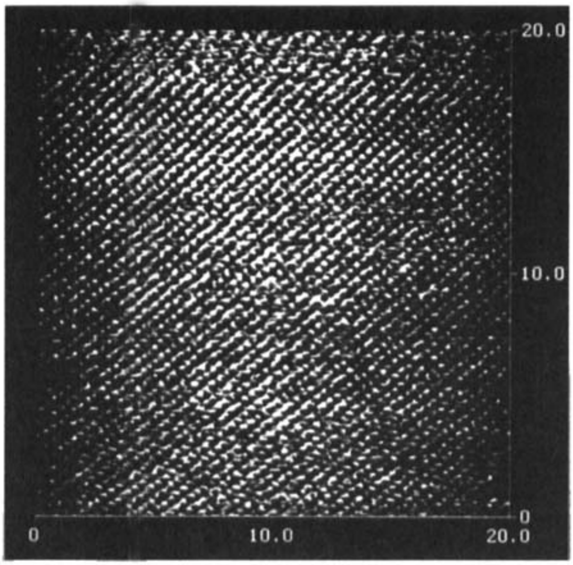

FIGURE 5 Contact AFM image of 20 nm scan.

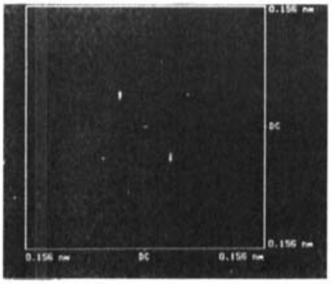

FIGURE 6 2D-FT sepctrum of Fig. 5.

CONCLUSIONS

We constructed high-quality monolayer films using a novel long-chain alkyl derivative $C_{37}H_{50}N_4O_4$ which has dinitrobenzene moiety(acceptor unit) and dihydrophenazine one (donor unit) bridged by methylene group at constant distance and bond angle to behave as unimolecular photoelectric device. We succeeded in getting its molecular images by atomic force micoscopy.

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We thank Prof. T. Kato (Utsunomiya University) for his manufactureing of the gas-tight type microsyringe with synchronous motor for spreading the desired quantity of spreading solution onto the LB trough and helpful suggestions to prepare monolayer film under a constant strain compression. We thank also to Prof. H. Nakahara (Saitama University), Prof. K. Iriyama (The Jikei University School of Medicine), and Prof. T. Ishii (Tsurumi University) for their useful comments to get AFM images of monolayer film. This work was partially supported by a special fund to K. U. (1997) from Osaka Prefecture University for promotion of graduate school.

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