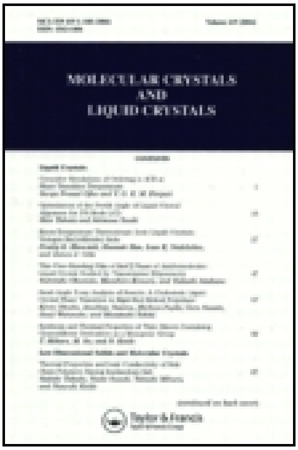

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Surface-Enhanced Raman Scattering Spectroscopy and AFM Studies of Amphiphilic Nitroaniline Derivatives

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To cite this article: Jung-Hyuk Im, Sung-Ho Park & Jae-Ho Kim (1997): Surface-Enhanced Raman Scattering Spectroscopy and AFM Studies of Amphiphilic Nitroaniline Derivatives, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 294:1, 59-62

To link to this article: http://dx.doi.org/10.1080/10587259708032248

Mol. Cryst. Liq. Cryst., 1997, Vol. 294, pp. 59–62
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SURFACE-ENHANCED RAMAN SCATTERING SPECTROSCOPY AND AFM STUDIES OF AMPHIPHILIC NITROANILINE DERIVATIVES

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ABSTRACT Surface-enhanced Raman scattering (SERS) Spectroscopy and atomic force microscopy (AFM) were employed to characterize the Langmuir-Blodgett (LB) monolayers of an amphiphilic nitroaniline derivatives, n-docosyl-2-methyl-4-nitroaniline (DCMNA) on both Ag surface and mica. DCMNA formed a stable, organized and homogeneous monolayer at the air-water interface only under the specific conditions. Structural changes at the interface induced by surface pressure, temperature and pH of the subphase, and the mole ratio of mixed molecules have been studied. The stable monolayers of DCMNA were obtained on a neutral subphase maintained lower than 10 ℃. The compressibility of the monolayer was improved by addition of arachidic acid or spreading the monolayer on an alkaline subphase. Micro-Raman and AFM studies indicated that pure DCMNA on a neutral subphase spontaneously formed a well ordered crystalline phase as well as an organized monolayer even under a lower surface pressure. AFM and lateral force microscopy (LFM) confirmed the arachidic acid minimizes self-aggregation of DCMNA and induces formation of monodispersed nano sized domain in the mixed monolayer.

INTRODUCTION

Nitroaniline moiety containing organic compounds have generated considerable interests for nonlinear optical applications due to their large second and third order nonlinear susceptibilities as well as their distinctive features, such as easy processability to various forms and controlling size of the materials. Langmuir-Blodgett (LB) technique has proven to be an effective method for construction of the organic superlattice with the required noncentosymmetric structure due to its unique advantages over the required noncentosymmetric structure due to its unique advantages over the conventional thin film methods such as precise controlled molecular orientation and thickness; elimination of the problems associated with spontaneous relaxation of the nonlinear optical (NLO) chromophore in the host-guest structure required noncentosymmetric structure due to its unique advantages over the conventional thin film methods such as precise controlled molecular orientation and thickness; elimination of the problems associated with spontaneous relaxation of the nonlinear optical (NLO) chromophore in the host-guest structure. In order to utilize particular advantages of the LB technique in fabrication of the organic noncentrosymmetric supermolecular structure containing DCMNA(n-docosyl-2-methyl-4-nitroaniline), it is essential to determine the optimum condition for formation of the monolayer at the air-water interface and for transferring to a solid substrate. Furthermore, it requires to establish the analytical methodology for probing structure of the monolayer and molecular interactions in the organized domain.

In the present study, we report on AFM and SERS spectroscopic studies carried out to elucidate the aggregation, orientation, and structure of DCMNA LB films at the air-water interface and on solid substrates.

EXPERIMENTALS

DCMNA was synthesized by n-alkylation reaction to MNA with docosylbromide. SERS spectra were collected using a triple monochromator coupled with a blue intensified CCD (Charge-Coupled device) array detector (Spex Industries, Edison, NJ,USA) and 514.5 nm lines of an Ar^+ laser (Coherent Co., Santa Clara, CA,USA) as an excitation sources. Thermally evaporated thin Ag films on mica under 1.0 x 10^{-6} torr were used for SERS substrates. A circular Teflon Langmuir trough (Mayer Feintechnik, Göttingen, Germany) was used to measure surface pressure-area isotherm and to prepare the LB film on the solid substrates. AFM micrographic images were obtained by normal contact-mode measurement with a V-shaped silicon nitride cantilevers. (spring const.:0.067 N/m, PSI-LS, Sunnyvale, CA,USA)

RESULTS AND DISCUSSION

Surface pressure-area (Π-A) isotherms in Figure 1-a indicated that pure DCMNA formed a stable monolayer at 8 ℃, and collapsed at relatively lower surface pressure due to weak amphiphilicity and strong aggregation tendency of MNA. The stability of the DCMNA monolayer at the air-water interface as well as the transfer efficiency to a solid substrate were significantly improved by forming mixed monolayers of DCMNA with AA(arachidic acid) at different mole ratios. Figure 1-b appeared that at a mole ratio of 1:1 the compressibility was increased by 25 mN/m comparing to the pure DCMNA monolayer.

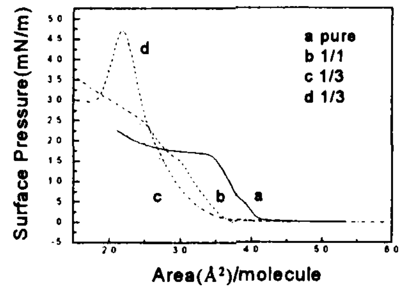

Figure 1. Π-A isotherms of pure and mixed DCMNA monolayers (mole ratio; DCMNA/AA) at 8 ℃ on pure water subphase (a-c), pH 12.0 subphase (d).

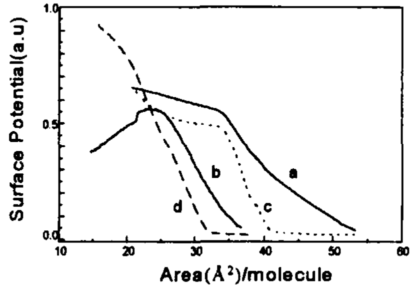

Figure 2. Surface potential-area isotherms of pure (a), mixed (b) DCMNA monolayers. Π-A isotherms of each monolayers are (c), (d) respectively.

However, surface potential-area isotherms in figure 2-b indicates that the mixed monolayer was also collapsed near 15 mN/m and the molecular orientation at the air-water interface was not significantly affected by existence of AA in the monolayers. Thus arachidic acid only improves the stability of monolayer and effectively disperses DCMNA at the interface. As shown in Figure 1-d, the stability of DCMNA monolayer also increased by strong electrostatic interaction with the alkaline subphase without significant changes its orientation at the interface. AFM and LFM images in Figure 3 demonstrated that AA and DCMNA are segregated and formed a few hundred nanometer scale domains in the mixed monolayer. Even at a relatively high surface pressure the DCMNA crystalline phase was not observed in the mixed monolayer. These results are consistent with the Π-A and surface potential-area isotherms. The optical micrograph and SERS spectra of pure DCMNA LB film on an Ag film showed three distinctive regions as shown in figure 4. Micro-Raman spectra of each regions indicated that region(1) has different structure from regions(2) and (3). The spectrum in Figure 4-(1) indicates that the region (1) consists of crystalline-like solid. On the other hand, spectra of regions (2) and (3) are the typical SERS of organized monolayer of pure DCMNA. Both spectra of (2) and (3) show strong bands from υ (C=C) in benzene ring at 1610 cm^{-1}, and for δ (NO_2) at 802 cm^{-1}, the strong, splitted band from υ (NO_2) at 1329 cm^{-1} due to non hydrogen bonded nitro group in the molecule. These spectral features in the region (2), and (3) demonstrate that MNA moiety directly contacts with the Ag surface through NO_2 group with tilted orientation, and well organized molecular arrangement exists.

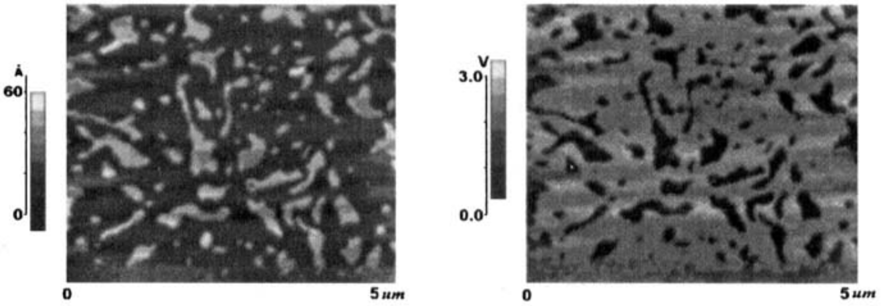

Figure 3. AFM and LFM images of DCMNA/AA(1/1) mixed monolayer on mica. (transfer pressure: 7mN/m).

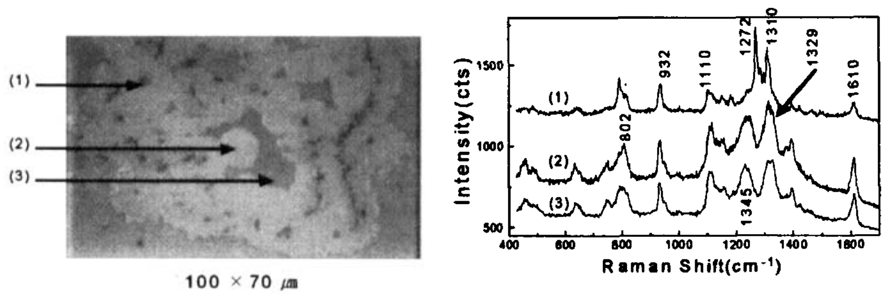

Figure 4. Optical micrographic image and SERS spectra of each designated spots.

In conclusion, a stable DCMNA LB monolayer can be constructed on solid surfaces under the controlled F such as pH, surface pressure, addition of inert matrix molecules. SERS and AFM studies indicated that the monolayer and self organized crystalline phase of DCMNA were coexisted in pure system, whereas in the mixed system uniformly dispersed segregated domain of well organized monolayers of pure DCMNA and AA were formed without noticeable crystalline phase.