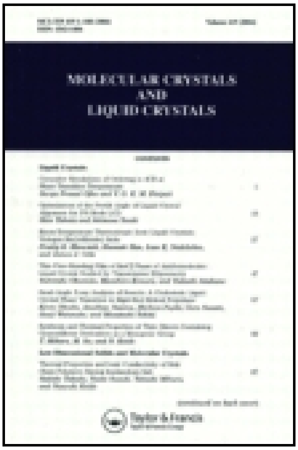

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Structural Characterization of LB Films of a Novel Azobenzene Compound: Ftir Evidence of a Two-Dimensional Hydrogen-Bonded Structure

Jiang Zhao [a] , Zhongyun Wu [a] , Jin Zhang [a] , Tag Zhu [a] , Abraham Ulman [a] [b] & Zhongfan Liu [a]

[a] Centre for Intelligent Materials Research (CIMR), College of Chemistry and Molecular Engineering, Beijing, 100871, CHINA

[b] Department of Chemistry, Polymer Research Institute, Polytechnic University, Brooklyn, New York, 11210, U.S.A.

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STRUCTURAL CHARACTERIZATION OF LB FILMS OF A NOVEL AZOBENZENE COMPOUND: FTIR EVIDENCE OF A TWO-DIMENSIONAL HYDROGEN-BONDED STRUCTURE

JIANG ZHAO, ZHONGYUN WU, JIN ZHANG, TAO ZHU, ABRAHAM ULMAN[a], and ZHONGFAN LIU*
Centre for Intelligent Materials Research (CIMR), College of Chemistry and Molecular Engineering, Beijing 100871, CHINA
a: Department of Chemistry and Polymer Research Institute, Polytechnic University, Brooklyn, New York 11210, U. S. A.

Abstract LB films of a novel azobenzene derivative were fabricated and characterized by AFM, Raman microscopy, and polarized transmission FTIR spectroscopy. The AFM and Raman microscopic data revealed a well-ordered uniform structure of the film, and the dichroism in two perpendicular polarized FTIR suggested that there exist two types of hydrogen-bonded carboxyl groups, which are orientated in planes perpendicular to each other, forming a two-dimensional inter-molecular hydrogen-bonded structure in the LB film.

Highly organized Langmuir-Blodgett (LB) films have attracted much attention during last decades because of their prospective applications in fabricating molecular electronic and photonic devices[1]. To realize and stabilize highly-ordered molecular array inside the monolayer, it is very important to introduce specific interactions[2], such as hydrophobic interactions between alkyl chains, aromatic interactions between π-conjugation systems, and hydrogen bonding between specific groups. In this paper, we design a novel azobenzene molecule, 4-didodecylamino-4'-(3-carboxypropyl)azobenzene, which is expected to form a well-organized layer structure in its LB films due to the co-existence of all the three kinds of molecular interactions mentioned above.

The π-A isotherm of the monolayer on air/water interface was measured at 20°C, which has a rather large slope in the linear region (~367 $mN{\cdot}m^{-1}{\cdot}nm^{-2}$) and a very high collapse pressure (~46mN/m), indicating that the title molecule can form a nice monolayer on the subphase. The azobenzene LB monolayers were fabricated by standard method,[1] at a surface pressure of 20 mN/m and a temperature of 20°C, and Z-type multilayers were obtained.

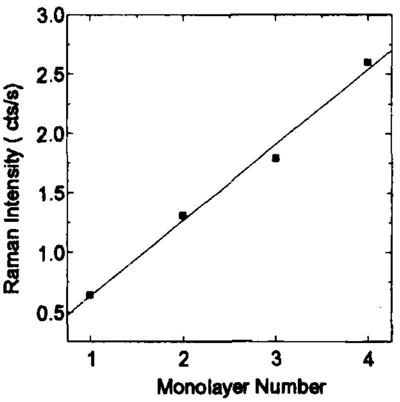

FIGURE 1 Dependence of Raman intensity at 1141 cm^{-1} of ν(ϕ-N) on the monolayer number.

To examine the structure of the LB film, atomic force microscopy (AFM), Raman microscopy and polarized FTIR spectroscopy were used. The morphological studies by AFM on the monolayer deposited on mica revealed its domain structure, in which the domains with size of 2μm×3μm and pinholes with size less than 0.2 μm in diameter were observed. The lateral uniformity of the LB film was also evidenced by the nearly identical Raman spectral features (i.e., peak positions and intensity) obtained from different sites on a 3-layer sample with a spatial resolution of ca. 1 μ m. On the other hand, the good order of interlayer packing for multilayer sample was demonstrated by the linear dependence of Raman intensity on the monolayer number, shown in Fig. 1. These data show that the azobenzene molecule adopted can form well-orderd LB monolayers, and make it essentially important to investigate the inter-molecular structure of the monolayer.

For structural characterization, FTIR spectra were measured with a Perkin-Elmer System 2000 FTIR spectrometer, equipped with a TGS detector, with the resolution of 4 cm^{-1}. Figure 2 is the polarized transmission spectra of the 9-monolayer LB film on CaF_2 substrate, which were taken with an incident radiation polarized parallel to (a) and perpendicular to (b) the dipping direction, respectively. Attention was paid on the two absorption bands of the carboxyl group, located in the frequency ranges of 1690-1710 cm^{-1} and 1405-1415 cm^{-1}, corresponding to the stretching vibrating mode of its carbonyl group (ν(C=O)) and the in-plane bending vibrating mode of its hydroxyl group (δ(OH, ip)), respectively. The peak position of ν(C=O) for parallel polarization was 1694 cm^{-1}, while for perpendicular polarization, it was 1708 cm^{-1}. This dichroism implies that the carbonyl groups were located in different microenvironments, or say, two different types of carbonyl groups were existing in the LB film. Generally, the frequency of ν(C=O) in free carboxyl group falls into a range of 1735-1760 cm^{-1}. When the COOH group is in a hydrogen-bonded environment, the ν(C=O) vibration shifts to lower frequency, and the stronger the hydrogen bond is, the lower frequency the ν(C=O) peak has[3]. Obviously, the C=O groups in the LB monolayers were all in the hydrogen-bonded states, but the bonding strength with the adjacent OH groups was not the same: the C=O group with its projection on the substrate surface being along the dipping direction was in a stronger

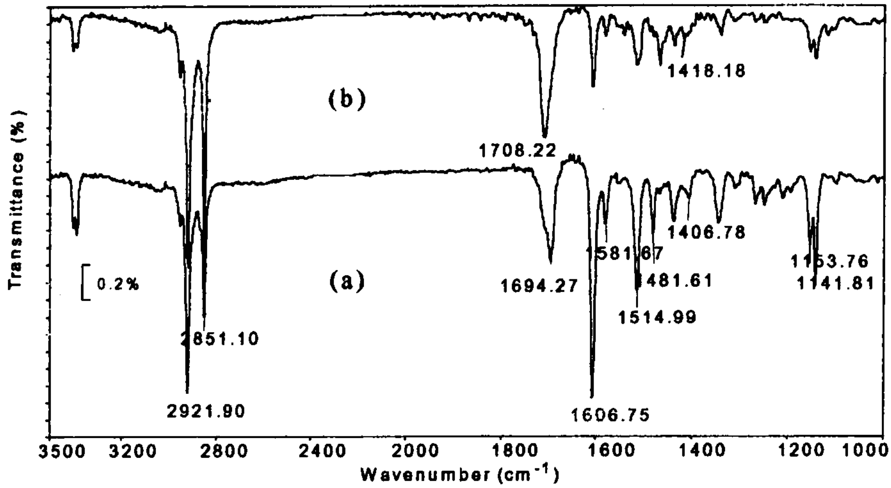

FIGURE 2 Polarized FTIR transmission spectra of a 6-monolayer azo LB film on CaF_2 substrate. (a): Polarization parallel to the dipping direction; (b): Polarization perpendicular to the dipping direction.

hydrogen-bonded state than that along the direction perpendicular to dipping. Similar conclusion can also be drawn by analyzing the in-plane bending vibration of OH group (δ (OH, ip)) of COOH group, at 1407 and 1418 cm^{-1} for parallel and perpendicular polarization, respectively. The δ(OH, ip) vibration shifts to higher frequency when the strength of its hydrogen bond gets stronger[3]. Combining the C=O and OH spectral data, we can imagine that in such monolayers, the C=O and OH of the COOH group are all in the hydrogen-bonded states: the C=O group parallel to the dipping direction forms a strong hydrogen bond with the OH group perpendicular to the dipping; whereas the OH group parallel to the dipping direction forms a weak hydrogen bond with the C=O group perpendicular to the dipping direction.

To obtain more experimental evidence, the polarization angle dependence of the FTIR spectra was studied. The intensity of ν(C=O) at 1694 cm^{-1} was found to have its maximum around 0° and reaches its minimum around 90°, while the intensity at 1708 cm^{-1} have its minimum around 0° and gets to its maximum around 90°. By numerical simulation, the orientation angles of the ν(C=O) transition dipoles at 1694 cm^{-1} and 1708 cm^{-1} were found to be -2° and 87°, respectively, referring to the dipping direction. This indicates that two differently hydrogen-bonded C=O groups are orientated nearly perpendicular to each other. The above dichroism phenomenon of the C=O and OH vibrations of the carboxyl group was also observed in LB films having different monolayers. Apart from the FTIR data, UV-Visible spectrum of LB monolayer shows

~40 nm blue-shift of absorption peak around 380 nm corresponding to the π-π* transition comparing with that for solution, indicating the existence of aggregation in monolayers.

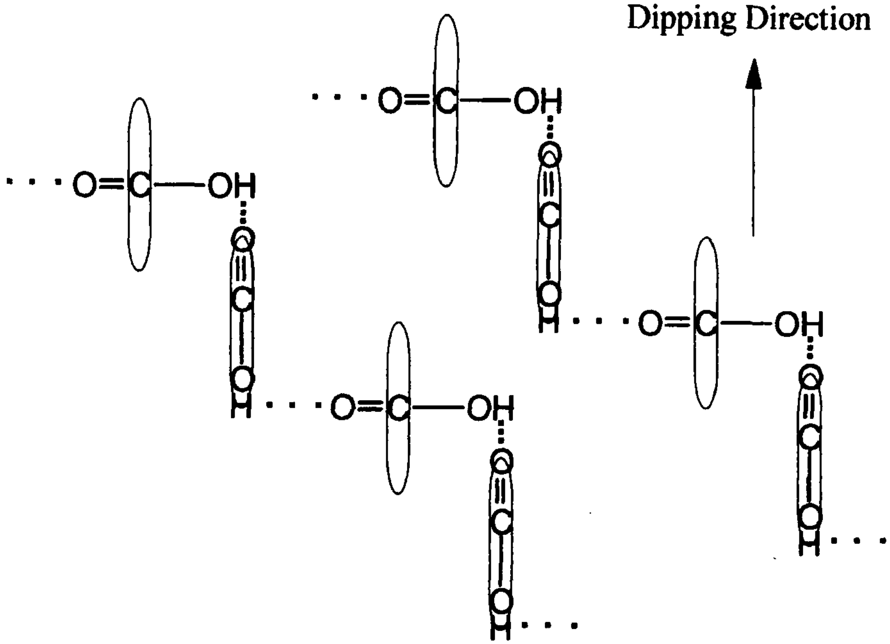

FIGURE 3 Projection of the two-dimensional hydrogen-bonded structure on the substrate surface, where the narrow rectangles represent the azobenzene group.

Figure 3 illustrates the possible structural model of the LB monolayer, showing the projection of the two-dimensional hydrogen-bonded COOH on the substrate surface. For simplicity, the molecular backbone was omitted. In this model, each COOH group links two other COOH groups of different molecules via H-bonds and the adjacent H-bonded COOH groups are perpendicular to each other in projection, leading to a zig-zag structure. Such a structural model gives a satisfactory explanation of our FTIR results.

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