Nonlinear Optical Properties of Langmuir-Blodgett Films from Two Crowned Azobenzenes

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Two crowned azobenzene derivatives APCM and APCN were synthesized and incorporated into a β-cyclodextrin derivative ACD. Both APCM/ACD and APCN/ACD formed a stable Langmuir monolayer at the air-water interface. Multilayer Langmuir-Blodgett (LB) films with an ordered lamellar structure were constructed from APCM/ACD and APCN/ACD monolayers which showed a nonlinear polarisability (β) of 4×10^{-29} and 1×10^{-30} esu, respectively, after a month of storage.

Azobenzene and its derivatives are of currently interest in terms of their potential application as information storage systems,[1] photochemical switching systems,[2] and more recently a novel type of Langmuir-Blodgett (LB) film materials with second-order nonlinear optical (NLO) properties.[3] By attaching crown ether groups to the azobenzene system, we synthesized two crowned azobenzene derivatives 4-aza-15-crown-5-4'-methoxyazobenzene (APCM) and 4-aza-15-crown-5-4'-nitroazobenzene (APCN) in expectation that the construction of multilayers could be facilitated because of complexation of crown rings with ions in the subphase. Here, we report the Langmuir monolayer and multilayer LB film formation, structural characterization and second-order NLO properties of the two crowned azobenzenes.

The crowned azobenzenes APCM and APCN were synthesized by conventional diazo-coupling reaction of 4-substituted aniline with N-phenyl-monoaza-15-crown-5.[4] To facilitate Langmuir monolayer formation APCM and APCN were incorporated in heptakis(6-undecylamino-6-deoxy)-β-cyclodextrin (ACD) which was synthesized in a similar manner as reported previously.[5]

ACD can form a stable monolayer at the air-water interface due to its hydrophilic cyclodextrin ring and hydrophobic long alkyl chains. But APCN and APCM alone can not owing to the lack in hydrophobic groups. However, if they are incorporated in ACD stable Langmuir monolayers can also be formed. The surface pressure-area (π-A) isotherms for ACD and the equimolar mixture APCN/ACD and APCM/ACD in pure water subphase are shown in Figure 1. The curves of APCN/ACD and APCM/ACD overlap each other and almost overlap with that of ACD. It indicates that APCN and APCM have been incorporated in the cavity of ACD for otherwise, the limited area of monolayers from APCN/ACD and APCM/ACD will be larger than that of ACD. The monolayers do not collapse until the surface pressure reaches 55 mN m^{-1}. The limited area of ACD obtained by extrapolating the condensed region to zero pressure is 230 Å^2. This value approximates to the theoretically calculated area of β-cyclodextrin plane (220 Å^2). So it can be concluded that in the monolayer the ACD ring plane is parallel to the surface of the subphase while the seven long alkyl chains are perpendicular to the water surface. The steep slope in the π-A isotherms and the high collapse pressure establish that ACD, APCN/ACD and APCM/ACD have a good film-forming ability and form a tight molecular arrangement in their Langmuir monolayer in pure water subphase.

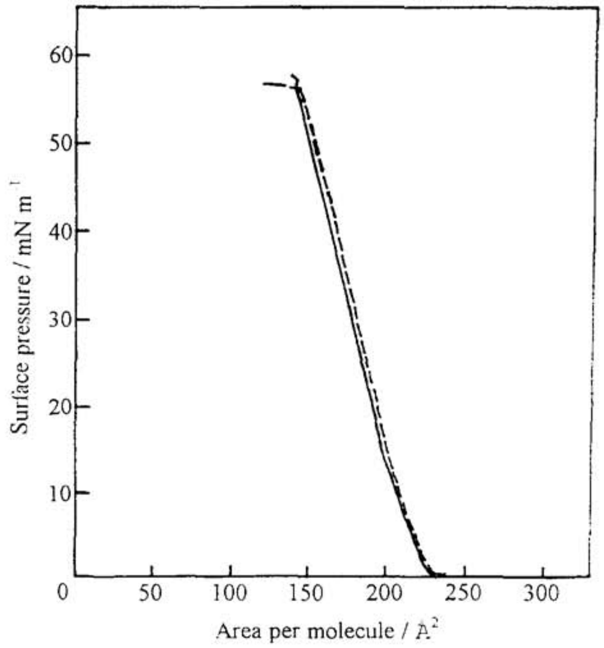

Figure 1. Surface pressure-area isotherms for ACD (—), APCN/ACD and APCM/ACD (······) in pure water subphase.

Changes of the molecular area with time for monolayers from ACD, APCN/ACD and APCM/ACD at a surface pressure of 30 mN m^{-1} in pure water subphase are quite small and apparently smaller than that of arachidic acid, indicating the good stability of the monolayers from ACD, APCN/ACD and APCM/ACD in pure water subphase.

The effect of pH of the subphase on the behavior at the air-water interface of monolayers from ACD, APCN/ACD and APCM/ACD has been investigated. Generally speaking, pH of the subphase does not show a significant effect on the behavior of ACD, APCN/ACD and APCM/ACD at the air-water interface though monolayers of APCN/ACD under a weak basic condition show a relatively high collapse pressure (> 55 mN m^{-1}).

Because crown ethers can complex metal ions in the subphase we have also investigated the effect of different amount of cadmium cation on the behavior of monolayers from ACD, APCN/ACD and APCM/ACD at the air-water interface. The results show that the optimum concentration of Cd^{2+} in the subphase is 10^{-5} – 10^{-4} mol l^{-1} for the construction of stable Langmuir monolayers from APCN/ACD and APCM/ACD.

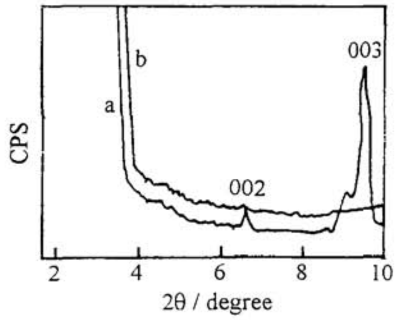

Figure 2. X-Ray diffraction of the 47-layered Z-type APCN/ACD LB film after stored for 28 (curve a) or 41 (curve b)days.

X-Ray diffraction patterns of the 47-layered Z-type LB film of APCN/ACD are shown in Figure 2. According to Bragg equation the thickness per layer of the film can be calculated. The value (27.29 Å) is larger than the molecular length of ACD (22.67 Å) estimated from the CPK molecular model due to the incorporation of APCN into ACD in which the crown ring moiety can not enter the cavity of ACD. Though having turned slightly disordered after storage for 28 days the LB film showed a good stability because it could still showed its X-ray diffraction signals (002 and 003) and the intensity of the diffraction signals increased in the order of 001 < 002 < 003. It indicates that the disorder of the LB film originated from the outer layer which was affected by factors such as air and light more directly. No X-ray diffraction signal was observed after the film was left for 41 days, establishing that the film had turned disordered. Considering that the film was assembled in pure water subphase, LB films of a higher stability could possibly be constructed through adjusting the subphase conditions, for instance, adding Cd^{2+} ion to the subphase or changing the pH value of the subphase.

The IR spectrum of a 100-layered ACD LB film constructed in pure water (pH = 6.5) subphase exhibits three characteristic absorption peaks at 2917 (ν_{CH2}^{as}), 2850 (ν_{CH2}^{s}), and 1041 cm^{-1} ($\nu_{C\text{-}O\text{-}C}^{as}$), respectively. The relationship between the intensity of the absorption peaks for the characteristic functional groups and the incident angle has been investigated by the polarized IR spectrum. The results exhibit that the maximum absorption angle approximates to zero degree. It indicates that the long hydrocarbon chains parallel each other and are perpendicular to the β-cyclodextrin plane.

Second-harmonic generation (SHG) of the Z-type Langmuir monolayer from APCM/ACD and APCN/ACD has been measured. According to the calculation and simulation results, the nonlinear polarisabilities (β) for APCM and APCN molecule are 4×10^{-29} and 1×10^{-30} esu, respectively. Both these two values are not high, compared with that of an azobenzene derivative $p\text{-}O_2N\text{-}C_6H_4\text{-}N{=}N\text{-}C_6H_4\text{-}p\text{-}N(CH_2CH_2)(CH_2CH_2OH)$ which has a similar molecular structure to APCN but a two order higher β value (5×10^{-28} esu)[6] than that of APCN. It seems inexplicable considering only from the molecular structure aspect. On the other hand, the SHG signal of a film depends on the arrangement of molecules in the film. For a certain compound, the more ordered for the arrangement of molecules in the film, the closer is the measured β value of the film to its real β value. If the arrangement of molecules is disordered, the SHG signals offset each other and the measured β value is low. Because the measurement of the second-order NLO response for both APCN/ACD and APCM/ACD LB film was conducted a month after their construction and the X-ray diffraction results showed that the 47-layered APCN/ACD LB film fabricated in pure water subphase had turned slightly or completely disordered after 28 or 41 days of storage, respectively, a relatively low β value was obtained for APCN/ACD LB film. However, for the LB film of APCM/ACD the measure β value is estimated to approximate to its real β value for most of the reported azobenzene molecules have a β value of the same order (10^{-29} esu).[3] This β value of 4×10^{-29} esu for APCM/ACD LB film is of great significance for the measurement of β was carried out a month after the fabrication of APCM/ACD LB film in a subphase containing Cd^{2+} and Na^{+} ion. It is concluded that the real β value of APCM molecules is 4×10^{-29} esu and the APCM/ACD film is so stable that its β value retains constant even after a month of storage. It is reasonable because APCN/ACD LB film fabricated in pure water subphase can be stable for almost a month and APCM/ACD LB film which was constructed in a subphase containing Cd^{2+} and Na^{+} ion should show a higher stability. So multilayer LB films of high stability from crowned azobenzenes may be fabricated to satisfy practical applications.

In conclusion, by incorporation into a new β-cyclodextrin derivative ACD both crowned azobenzenes APCM and APCN form a stable Langmuir monolayer at the air-water interface. Transfer of the monolayers onto solid substrates gives multilayer LB films with an ordered lamellar structure. SHG measurements show that the nonlinear polarisability (β) of the LB film from APCN/ACD in pure water subphase and APCM/ACD in a subphase containing Cd^{2+} and Na^{+} ion reaches 1×10^{-30} and 4×10^{-29} esu, respectively, after a month of storage.

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