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Evaluation of Anisotropic Photoresponses in Ultrathin Organic films by a Highly Sensitive Polarized Optical Waveguide Method

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EVALUATION OF ANISOTROPIC PHOTORESPONSES IN ULTRATHIN ORGANIC FILMS BY A HIGHLY SENSITIVE POLARIZED OPTICAL WAVEGUIDE METHOD

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Abstract Highly sensitive polarized absorption measurement by the optical waveguide (OWG) detection system was made to analyze the orientation of photogenerated radicals in Langmuir-Blodgett (LB) films. The extinction coefficient changes upon photoexcitation of specific ion-pair charge-transfer complexes between two kinds of amphiphilic 4,4'-bipyridinium and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate were estimated by this system. Amphiphilic 4,4'-bipyridinium ions in LB films deposited directly on an OWG showed different anisotropy from those deposited on an OWG covered with three monolayers of cadmium arachidate. The structure of substituents also affected the orientation.

INTRODUCTION

Organized monolayers containing ordered chromophores are interesting for their specific physical properties and a variety of technological application. We have reported unique photoresponses of specific ion-pair charge-transfer (IPCT) complexes of 4,4'-bipyridinium salts with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($TFPB^-$). Irradiation of an IPCT band in an inert atmosphere caused photoinduced electron transfer from a donor $TFPB^-$ to an acceptor 4,4'-bipyridinium ion accompanied by remarkable colour changes from pale yellow to blue.[1] Different orientation of photoinduced 4,4'-bipyridinium radical cations depending on the structure of substituents was observed in LB films with 120 monolayers by a conventional polarized absorption spectroscopy.[2]

The evanescent waves of the optical waveguide (OWG) have been used to sensitively detect and to characterize adsorbates and the optical properties of thin films.[3] We applied this method to sensitively detect photoreactions in ultrathin films.[4]

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Recently, we have reported the analysis of optical characteristics of 4,4'-bipydinium polymer thin films by the highly sensitive OWG polarized detection system.[5] In the present paper, the orientation of photogenerated 4,4'-bipyridinium radical cations in LB films with only 1～5 monolayers analyzed by similar method will be reported.

EXPERIMENTAL

$TFPB^-$ salts of two amphiphilic 4,4'-bipyridinium derivatives with different alkyl substituents (HV^{2+}, AV^{2+}) as shown in Figure 1 were used. LB films of HV^{2+} or AV^{2+} in a 1:4 mixture with arachidic acid (AA) were deposited on the surface of a thermaly K^+-exchanged OWG,[4] or on the OWG covered with three monolayers of cadmium arachidate.

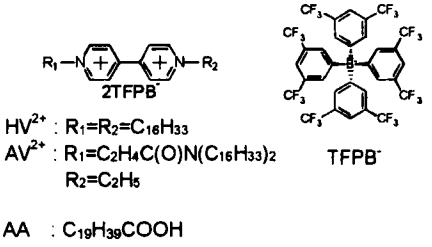

FIGURE 1 Structure of bipyridinium salts (HV^{2+}, AV^{2+}) and arachidic acid (AA)

The refractive index profile of the OWG was assumed as the Gaussian. The complex propagation constants were calculated by solving the wave equation based on the multilayer approximation as reported previously.[5] The imaginary part of the complex propagation constant obtained by such calculation causes the absorption of guided wave. The refractive index changes of thin films, which were caused by extinction coefficient changes upon photoexcitation, were included in this calculation.

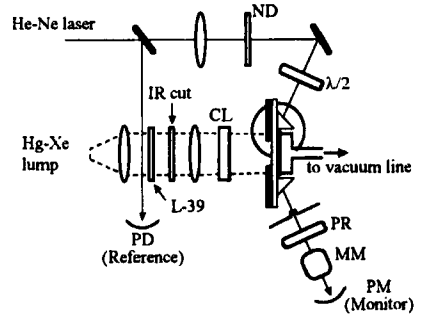

FIGURE 2 Schematic diagram of the polarized OWG detection system with excitation.

LB films deposited on the OWG were degassed by a rotary pump in a small chamber and irradiated with a Hamamatsu 150 W Xe-Hg lamp through Toshiba IR-cut and L-39 filters (>365 nm). The guided waves of TE_0 and TM_0 modes were induced by introducing a He-Ne laser (632.8 nm) beam whose polarization was rotated by a half wave plate. The guided waves taken out from the OWG were detected by a photomultiplier (PM) through a polarizer. The irradiation and polarized OWG detection systems are schematically shown in Figure 2.

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RESULTS AND DISCUSSION

Specific orientation of many chromophores has been observed in LB films by conventional polarized absorption, Electron Spin Resonance, second harmonic generation and other methods. The orientation of photogenerated radicals in LB films of AV^{2+} and HV^{2+} with arachidic acid were also found to be controlled by the substituents of 4,4'-bipyridinium ions.[2] From the conventional polarized absorption method, the orientation angles of photogenerated radicals of HV^{2+}/AA and AV^{2+}/AA in LB films with 60×2 monolayers deposited on quartz plates were reported as 45°~46° and 89°, respectively.[2] The anisotropic orientation in LB films with a few monolayers can be analyzed with the polarized OWG absorbance data. If the transition dipole moments make an angle θ to the surface normal of OWG and their projections on OWG are randomly distributed,

$$\theta = \tan^{-1}\sqrt{2k_{TE}/k_{TM}} \qquad (1)$$

where k_{TE}, k_{TM} are the extinction coefficients of TE_0 mode and TM_0 mode. The extinction coefficient changes upon irradiation for LB films of AV^{2+}/AA directly deposited on the OWG are shown in Figure 3. Such changes are due to the formation of 4,4'-bipyridinium radical cations which show absorption at 632.8 nm. Considerable differences in the extinction coefficient between TE_0 and TM_0 were observed. The orientation angles of 4,4'-bipyridinium radical cations in LB films were obtained from these data using equation (1) as shown in Figure 4. In the case of LB films deposited on the OWG covered with three monolayers of cadmium arachidate, the orientation angle hardly changed with the number of monolayers, giving the average value of 43.1° for HV^{2+}/AA and 52.4° for

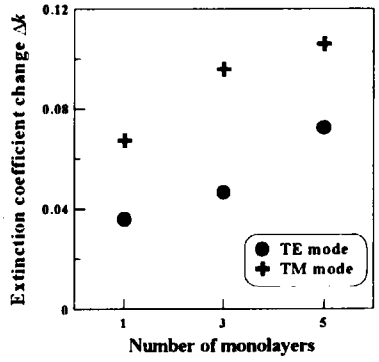

FIGURE 3 Extinction coefficients vs. the number of monolayers for LB films of AV^{2+}/AA directly deposited on OWG.

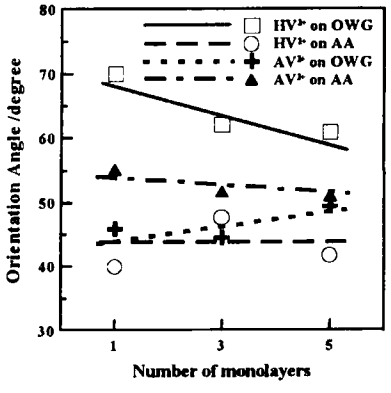

FIGURE 4 The orientation angles vs. the number of monolayers.

AV^{2+}/AA systems, respectively. Meanwhile the orientation depended on the number of monolayers in LB films directly deposited on the OWG. The HV^{2+}/AA system showed a clear decreasing tendency of orientation angle approaching the value observed for LB films with 60 monolayers on one side of a substrate. The AV^{2+}/AA system seemed to show an increasing tendency. FT-IR measurements revealed that stearic acid (SA) molecules in the first layer were oriented almost perpendicular to the substrate and that those in substrate layers in LB films up to 9 monolayers were tilted.[6] The observed orientation angles for 4,4'-bipyridinium radical cations in LB films directly deposited on the OWG corresponded to such observation for SA. Since long alkyl chains of HV^{2+} and AV^{2+} are expected to be aligned along AA molecules in LB films, the orientation of 4,4'-bipyridinium radical cations will be affected by the way how alkyl substituents are attached to HV^{2+} or AV^{2+}. 4,4'-Bipyridinium group in HV^{2+} having two hexadecyl chains symmetrically at its two ends will be oriented parallel to the substrate, while that in AV^{2+} having two hexadecyl chains at one end and an ethyl group at another end will be tilted. In LB films with 3 or 5 monolayers, the orientation of 4,4'-bipyridinium radical cations will be gradually changed according to the orientation change of AA molecules, which would be similar to SA.

CONCLUSION

The extinction coefficient changes of extremely thin LB films of two 4,4'-bipyridinium salts, $HV^{2+}(TFPB^-)_2$ and $AV^{2+}(TFPB^-)_2$ upon photoexcitation were estimated by highly sensitive polarized absorption detection system using OWG. These results showed that both substituents of 4,4'-bipyridinium ions and the nature of substrate surface affected the orientation of 4,4'-bipyridinium radical cations in LB films with a few monolayers.

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