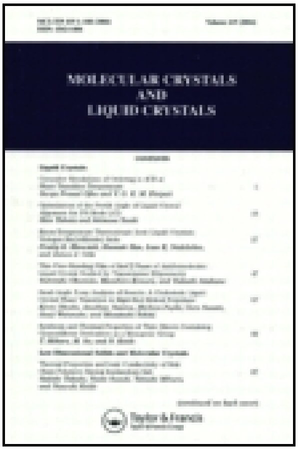

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Highly Sensitive Optical Waveguide Detection of Transient Species in Langmuir-Blodgett Films upon Pulsed Laser Excitation

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HIGHLY SENSITIVE OPTICAL WAVEGUIDE DETECTION OF TRANSIENT SPECIES IN LANGMUIR-BLODGETT FILMS UPON PULSED LASER EXCITATION

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Abstract Transient species upon pulsed laser excitation of ultrathin Langmuir-Blodgett (LB) films was detected sensitively by the optical waveguide (OWG) method. Amphiphilic tetraphenylporphyrin in mixed LB films with dioctadecyldimethylammonium at 1:5 and 1:50 were prepared on the surface of OWGs. These films were excited with the second harmonics of a ns Nd:YAG laser in degassed environment. Transient absorption of excited triplet porphyrins in LB films with only two monolayers was detected by the present method. It was about hundred times increase of sensitivity as compared with a conventional normal incidence measurement. Different decay dynamics were observed for excited triplet state porphyrins in LB films depending on the molar ratio, which was attributed to inhomogeneous distribution of chromophores.

INTRODUCTION

We have been studying various photoresponses of organized molecular assemblies as schematically shown in Figure 1 in order to construct novel molecular photonics devices. Among specific photoresponses we have achieved are ultrafast (<1 ps), persistent and reversible photoinduced electrochromism by specific ion-pair charge-transfer (IPCT) complexes of 4,4'-bipyridinium in various microenvironments, photon-mode spatial light modulation, and highly anisotropic photoconduction. We have shown that the linear and nonlinear photoresponses can be controlled at the molecular level in such organized systems. [1] It is very important to observe optical properties and photoresponses in ultrathin organic films in view of a sensing application with fast response and molecular photonics based on organized chromophores in Langmuir-Blodgett (LB) films.

Optical waveguides (OWGs) are essential components of advanced photonics and integrated optics. The electric fields of light propagating through the OWG layer have an exponentially decreasing value as evanescent waves beyond the both surfaces of the OWG. Evanescent waves have been used to sensitively detect and to characterize adsorbates and thin films on the OWG. Swalen et al. [2] measured optical absorbances of

LB films sandwiched between a glass and a polymer OWG with much higher sensitivity than conventional absorption measurements. Ito and Fujishima [3,4] applied the OWG method to detect photodeposition of Ag from aqueous solutions onto TiO_2 by flash photolysis and to observe electrochemistry of adsorbate.

Recently we have developed an OWG detection system for photoreactions in degassed environments.[5-7] Photoinduced electrochromism by specific IPCT complexes of 4,4'-bipyridinium in steady photolysis was detected even in a single monolayer LB film (2.7 nm thick) and in ultrathin polymer films by using the OWG method. A 150-fold increase in the sensitivity of the OWG method as compared with the conventional method was demonstrated from the colour change measurement in polymer films. In the present paper we will report extremely sensitive detection of transient species and decay kinetics in ultrathin LB films by the OWG method, which will contribute a great deal to elucidate the mechanism of photoresponses and to control them at the molecular level.

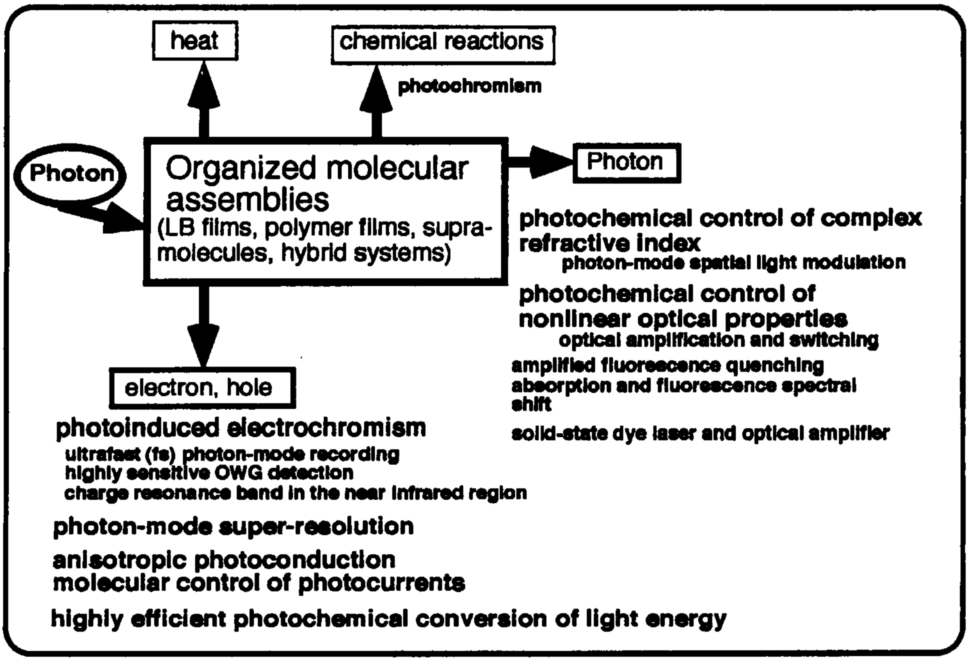

FIGURE 1 Schematic representation of specific photoresponses in organized molecular assemblies.

EXPERIMENTAL

Tetraphenyl-type amphiphilic porphyrin (ZnPC$_4$AB) was used in the present experiment. The structures of ZnPC$_4$AB and dioctadecyldimethylammonium bromide (2C18NB) are shown in Figure 2.

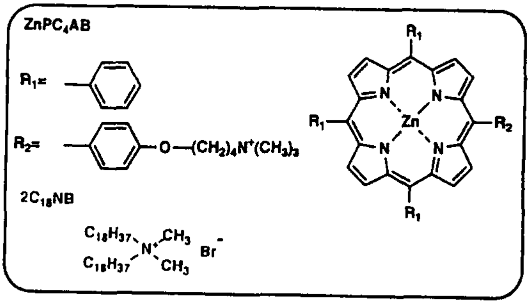

FIGURE 2 The structure and abbreviations of the compounds.

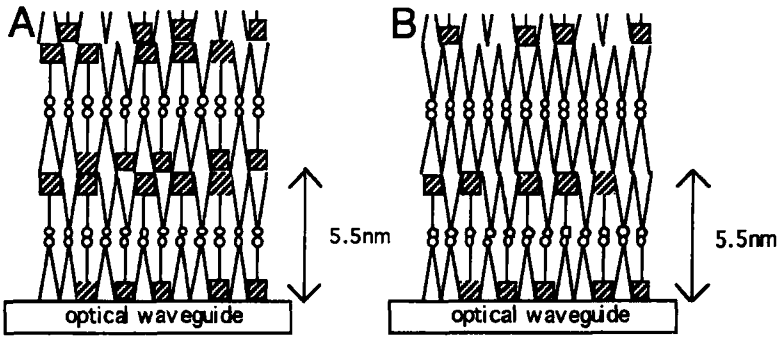

FIGURE 3 Two types of LB films employed in the present experiments.

LB films of ZnPC4AB and 2C18NB were formed on the surface of OWG glass prepared by a thermal ion-exchange method in molten KNO_3 at 370 ±1°C for 4 h. Monolayers (2 - 24) of ZnPC4AB in a 1:5 or 1:50 mixture with 2C18NB were deposited at 30 mN m^{-1} and 23°C to form LB films as polyion complexes with dextran sulfate on a hydrophobic surface of the OWG treated with a silane coupling agent. Two types of LB films, (A) usual Y-type and (B) alternate Y-type as schematically shown in Figure 3, were prepared for "highly sensitive detection measurements " and "kinetic studies", respectively. In film B face-to-face interactions of porphyrins at the excited state will be prevented by two monolayers of 2C18NB. These films were degassed by a rotary pump in a small chamber and irradiated with the second harmonics of a ns pulsed Nd:YAG laser (532.0 nm, 10 ns, 2 - 10 mJ/pulse) from a surface normal direction as shown schematically in Figure 4. The pulsed laser beam was focused to 2 mm x 20 mm area with convex and concave cylindrical lens to excite thin films between two coupling prisms. No damage of samples was observed by repeated excitation at 532 nm. Ar^+ laser, He-Ne laser, and diode lasers (670 - 830 nm) were used as probe light. The intensity of the OWG signal was detected with a photomultiplier through appropriate filters to cut 532 nm pulse and was recorded with a digital storage oscilloscope (Sony-Tektronix TDS540A, 8-bit A/D) with or without averaging. The transient absorbance (ΔAbsorbance) was calculated from the OWG signals after laser excitation relative to the average signal level before excitation.

Transient absorption spectra of ZnPC4AB in methanol upon ns laser excitation were observed with a streak camera (Hamamatsu Photonics C2830S).

RESULTS AND DISCUSSION

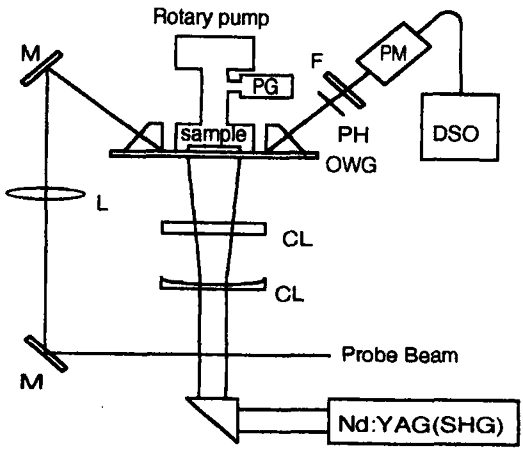

FIGURE 4 The block diagram of an OWG detection system for laser flash photolysis.

Chromophores in LB films only on one side of the substrate were excited in the OWG measurement. The dependence of the transient initial OWG absorbance upon ns laser excitation of a 1:5 LB films A with 16 monolayers on the wavelength of probe light is shown in Figure 5 together with the transient absorption spectra of ZnPC4AB in methanol solution 50 μs after excitation. They corresponded very well each other, which indicated that the transient absorption detected by the OWG method in LB films is attributed to the excited triplet porphyrin [7]. The transient absorbances monitored at 457.9 and 476.5 nm plotted against the number of monolayers showed almost a linear dependence. [7] The minimum transient absorbance detected in the present system with the 8 bit A/D is 1.7×10^{-3}. For the excited triplet of amphiphilic porphyrin (16.7 mol %) in 1:5 mixed LB films A, the detection limits were two monolayers.

The absorbance of LB films A containing ZnPC4AB with 2 - 24 monolayers at the excitation laser wavelength (532 nm) ranged from about 0.002 to 0.020. No transient absorption was observed even in LB films with 24 x 2 monolayers by the conventional normal incidence laser flash photolysis mainly due to the extremely small optical path length (total thickness is about 120 nm). Recently Tran-Thi et al. [8,9] reported the transient absorption measurements in LB films containing heterodimers of cationic porphyrin and anionic phthalocyanine upon excitation with ns and subpicosecond pulsed lasers at 532 - 565 nm. They prepared LB films with 150 - 400 monolayers on each side of a substrate and observed transient absorption or photobleaching with maximum absorbance changes of only about 0.02 - 0.08. Comparison of these results indicated much increased sensitivity of the present OWG method in time-resolved measurements as compared with the conventional method.

The decay curves are shown in Figures 6 and 7 for LB films B. In LB films B with a 1:5 ratio, the decay of triplet shown in Figure 6 followed neither first order nor second order kinetics. It followed a dispersive kinetics with a time dependence of $\exp(-ct^{0.2})$,

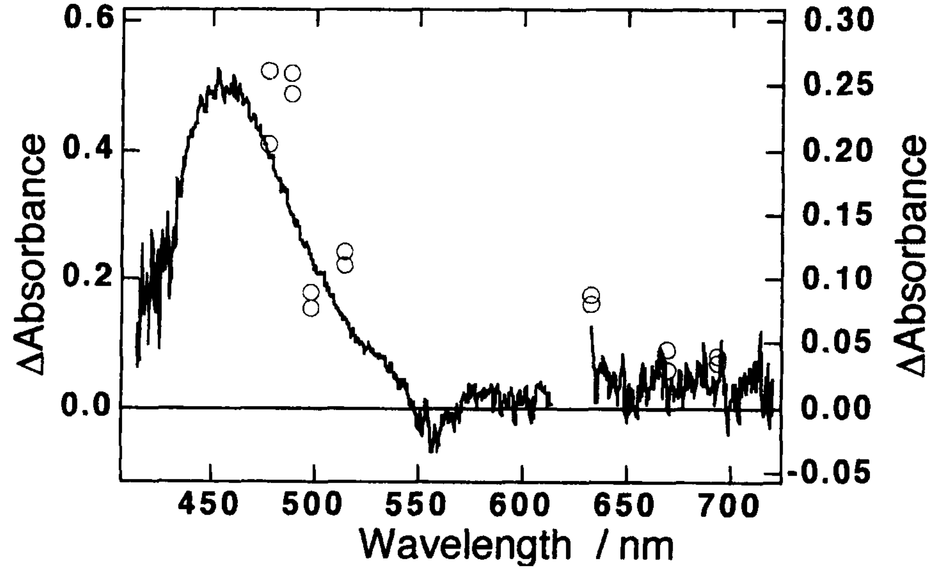

FIGURE 5 Wavelength dependences of transient absorption in LB films A by the OWG method (O) and that in methanol (---) upon ns laser excitation at 532 nm.

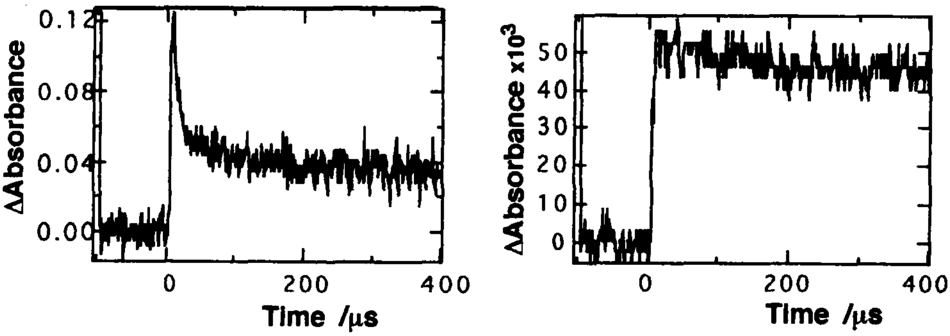

FIGURE 6 Decay of transient OWG absorbance at 476.5 nm in 1:5 LB films.

FIGURE 7 Decay of transient OWG absorbance at 476.5 nm in 1:50 LB films.

which indicated that the microenvironment and/or the intermolecular interaction of excited porphyrins are not identical in LB films. A fast decaying component disappeared in a 1:50 LB films B as shown in Figure 7. At longer time scale the decay is still not single exponential and followed a dispersive kinetics with a time dependence of exp(-ct $^{0.5}$) as shown in Figure 8. Since face-to-face interactions of porphyrins in hydrophobic regions are prohibited in B-type LB films studied, these results indicated inhomogeneous in-plane distribution and interactions of porphyrins even in 1:50 mixed LB films.

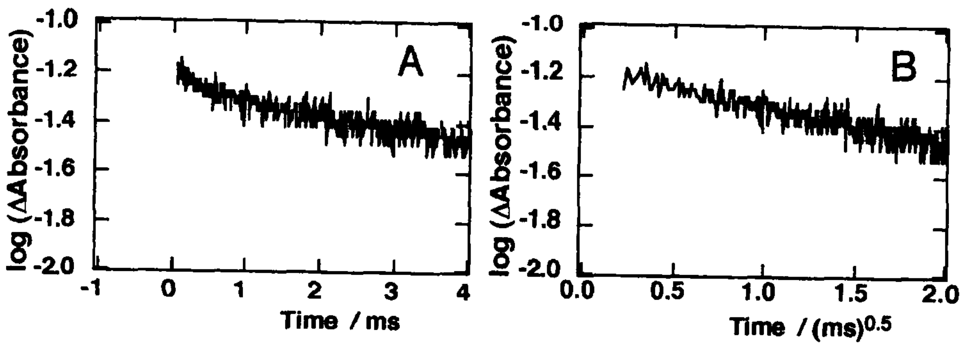

FIGURE 8 Decay of transient absorbance at 476.5 nm in 1:50 alternate Y-type LB films; (A) first order plot, (B) dispersive plot.

CONCLUSION

The OWG method was shown to sensitively detect transient species in ultrathin films upon ns laser excitation. It is very useful to elucidate and to control the photoresponses at the molecular level. It will become possible to discuss the dynamics even in a single monolayer LB films by the present OWG method with a time resolution of about 100 ps.

ACKNOWLEDGMENTS

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