Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 15 Jul 2010

To cite this article: Hideki Kawai, Kazuhiro Nakano & Toshihiko Nagamura (2003): HIGHLY SENSITIVE MEASUREMENTS OF TRANSIENT ABSORPTION SPECTRA OF ULTRATHIN ORGANIC FILMS BY THE WHITE LIGHT OPTICAL WAVEGUIDE METHOD, Molecular Crystals and Liquid Crystals, 406:1, 163-168

To link to this article: http://dx.doi.org/10.1080/744819000

Mol. Cryst. Liq. Cryst., Vol. 406, pp. 163/[357]–168/[362], 2003

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390263361

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HIGHLY SENSITIVE MEASUREMENTS OF TRANSIENT ABSORPTION SPECTRA OF ULTRATHIN ORGANIC FILMS BY THE WHITE LIGHT OPTICAL WAVEGUIDE METHOD

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White light optical waveguide (WOWG) method was applied to measurement of transient absorption spectra of ultrathin polymer and Langmuir-Blodgett (LB) films. Tetraphenylporphyrin derivatives in poly(methyl methacrylate) films and in a mixed LB films with arachidic acid were prepared on the surface of OWG glasses. The WOWG method has two orders of magnitude higher sensitivity than the conventional absorption method. The transient absorption changes of intramolecular electron transfer reactions between porphyrin and viologen were detected highly sensitively in ultrathin films by the WOWG method.

Keywords: LB film; optical waveguide; tetraphenylporphyrin; white light

INTRODUCTION

Optical waveguide (OWG) is one of the essential components in advanced photonics and integrated optics. The electric fields of light propagating through the OWG layer by repeated total reflection have an exponentially decreasing value as evanescent waves beyond both surfaces of the OWG layer. Evanescent waves have been used to sensitively detect and to characterize adsorbates and thin films on the OWG glass. Recently the OWG methods have been employed for spectroscopy using white light as a probe beam [1,2]. Kato *et al.* measured the absorption spectra of monolayer

This study was partly supported by the Grant-in-Aid for Scientific Research on Priority Areas "Molecular Synchronization" (No. 13022230) "Photofunctional Interface" (14050049), and Grants-in Aid for Scientific Research A (14205122) from the Ministry of Education, Science, Sports, and Culture, Japan.

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or sub-monolayer of Cu-porphyrin on the OWG glass [1]. Ohno *et al.* reported the absorption spectra of cytochrome *c* adsorbed on a quartz glass or gold surface were measured with evanescent wave of the non-contacted OWG layer [2].

We have been studying highly sensitive detection of various photoreactions and photoresponses in ultrathin organic films by the use of various types of laser as a probe in the OWG method [3–7]. Photoinduced electrochromism by specific ion-pair charge-transfer complexes of 4,4′-bipyridinium in steady photolysis was detected even in a single monolayer LB film (2.7 nm thick) and in spin-coated ultrathin polymer films [3,4,7]. Transient species upon pulsed laser excitation of ultrathin polymer films and LB films was also detected sensitively [5–7]. A 150 times increase was demonstrated in the sensitivity of the OWG method as compared with the conventional method. Recently, we have measured, for the first time, transient absorption spectra of ultrathin polymer films by a white light optical waveguide (WOWG) method using white light as a probe beam [8]. The WOWG method was shown to be useful for extremely high sensitive measurement of transient absorption spectra and decays in ultrathin film upon laser excitation. In this paper, we report the transient absorption measurements of intramolecular electron transfer reactions in ultrathin films using the WOWG method.

EXPERIMENTAL

OWG substrates were prepared according to the similar method reported previously [8]. The structures of tetraphenylporphyrin derivatives are shown in Figure 1. The LB films of $TPPC_nA$ in a 1:10 mixture with arachidic

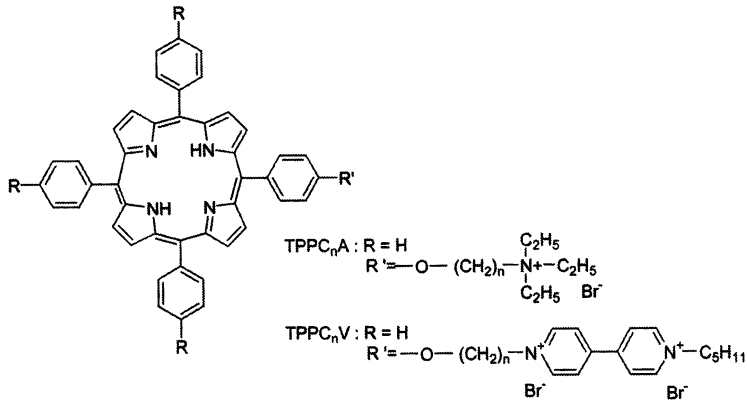

FIGURE 1 Structure and abbreviation of tetraphenylporphyrin derivatives.

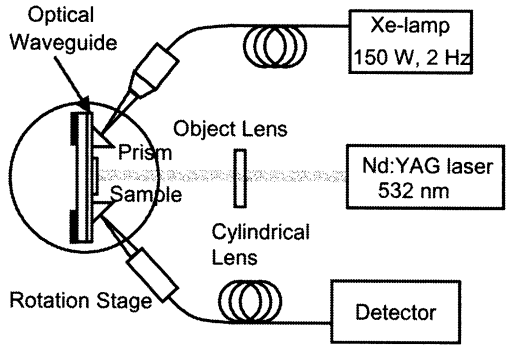

FIGURE 2 Schematic diagram of a WOWG detection system for transient absorption spectrum by nanosecond laser flash photolysis.

acid (AA) were deposited on the surface of OWG glass at 20 mN m^{-1} and 18°C. The subphase contained $CdCl_2$ (0.25 mM) and $NaHCO_3$ (0.05 mM). Ultrathin poly(methyl methacrylate) (PMMA) films containing $TPPC_nA$ or $TPPC_nV$ with a weight ratio of 500:1 were prepared by spin-coating.

The block diagram of the WOWG laser flash photolysis system is shown in Figure 2. The details of this system were reported previously [8]. The samples were excited with the second harmonics of a nanosecond pulsed Nd:YAG laser (532 nm) from a surface normal direction. The probe light was detected with a photomultichannel analyzer for steady absorption spectra, with a photomultiplier and a streak camera for transient absorption spectra.

RESULTS AND DISCUSSION

Absorption spectra of $TPPC_6A$/AA (1:10) LB film measured by the conventional spectrophotometer and the WOWG method are shown in Figure 3. The Q-band at 550–700 nm region was not observed clearly by the spectrophotometer, since its detection limit is about 0.0002. On the other hand, the same film measured by the WOWG method gave well-resolved four peaks of the Q-band as shown by the solid line. Comparison of the results shown in Figure 3 indicated the WOWG method has two orders of magnitude higher sensitivity than the conventional absorption method. Itoh *et al*. reported a relative sensitivity of the OWG systems was more than 100 times [9]. The WOWG method proved to be extremely sensitive for measurement of absorption spectra in a single monolayer LB film.

Time profile of transient absorption at 450 nm of the spin-coated $TPPC_6A$/PMMA film upon a nanosecond Nd:YAG laser at 532 nm is shown in Figure 4 (a). The transient absorption was attributed to the excited triplet

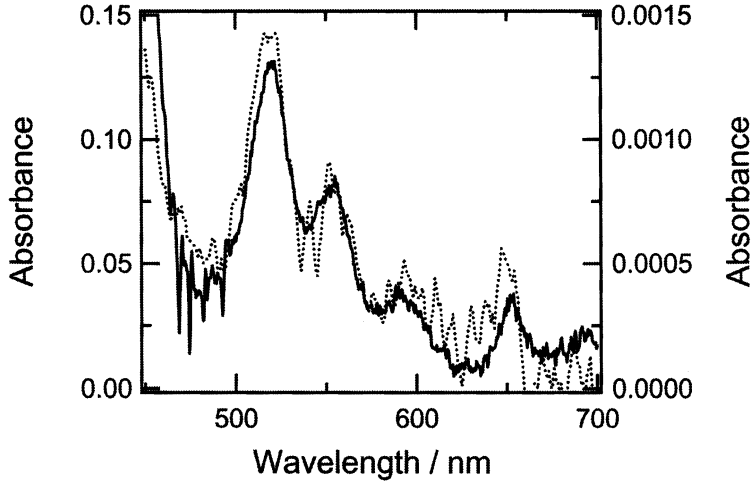

FIGURE 3 Absorption spectra of $TPPC_6A$/AA (1:10) LB film by a WOWG method (solid line, left axis) and a spectrophotometer (dotted line, right axis), respectively.

state of tetraphenylporphyrin. The lifetime of the excited triplet state of tetraphenylporphyrin was estimated to be 30 μs. The absorbance of the polymer film at the excitation wavelength was about 0.0005. No transient absorption was observed by the conventional normal incidence laser flash

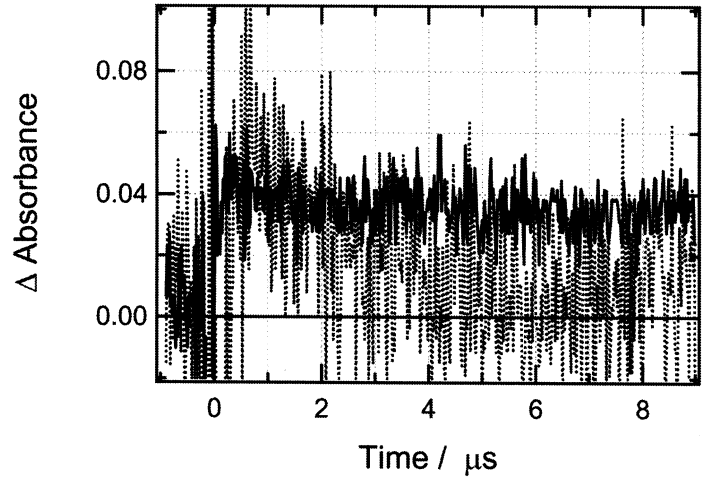

FIGURE 4 Time profile of transient absorption at 450 nm of (a) $TPPC_6A$/PMMA film (solid line) and (b) $TPPC_3V$/PMMA film (dotted line), excited with a 532 nm nanosecond laser.

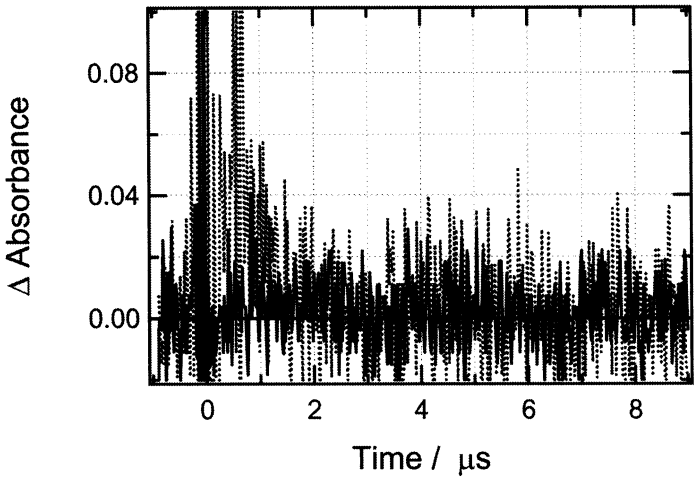

FIGURE 5 Time profile of transient absorption at 605 nm of (a) $TPPC_6A$/PMMA film (solid line) and (b) $TPPC_3V$/PMMA film (dotted line), excited with a 532 nm nanosecond laser.

photolysis. Figure 5 (a) shows the time profile of transient absorption at 605 nm of the $TPPC_6A$/PMMA film. No transient absorption was observed in the film at 605 nm. Similar transient absorption changes were observed in the spin-coated $TPPV_6A$/PMMA film. The lifetimes at 450 nm of the excited triplet state of $TPPC_6V$ were almost the same as that of $TPPC_6A$.

Time profile of transient absorption at 450 nm of the spin-coated $TPPC_3V$/PMMA film is shown in Figure 4(b). The transient absorption kinetics of $TPPC_3V$ followed single exponential decay with a lifetime of 1.8 μs. The effect of spacer length between porphyrin and viologen was demonstrated by more than 16 times decrease of the excited triplet state in porphyrin. The transient absorption of the $TPPC_3V$/PMMA film was observed at 605 nm as shown in Figure 5(b), which was attributed to viologen cation radical. These results strongly suggested that intramolecular electron transfer reactions were caused from porphyrin to viologen in the $TPPC_6V$/PMMA ultrathin film. The WOWG method was shown to be useful for extremely high sensitive measurement of an intramolecular electron transfer reaction in ultrathin films upon laser excitation.

CONCLUSION

The steady and transient absorption in ultrathin films were measured highly sensitively by the WOWG method. It is expected to give spectroscopic

and kinetic information on chromophores in organized thin film, which is essential to construct molecular photonics and electronic devices.

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