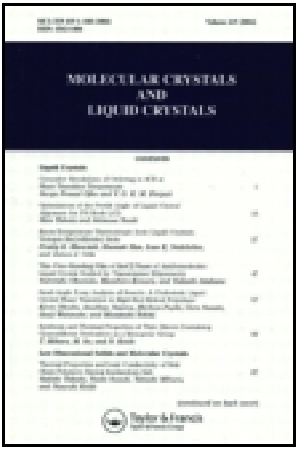

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Observation of Second Harmonic Signals from *cis*-Dialkoxyazobenzene Assisted by Molecular Interactions with Viologen Adsorbed at the Glass Surface

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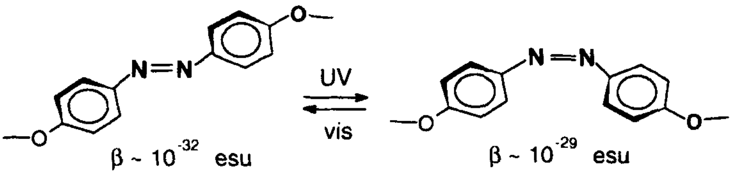
The second harmonic (SH) signal *cis*-dialkoxyazobenzene (*cis*-Azo) was obtained by using electrostatic molecular interactions with viologen (V) at the glass/liquid interface. Comparison of SH signal profiles between *cis*-Azo-V linked- and nonlinked molecular systems verified the presence of adsorption equilibrium between the two chromophores.

Keywords: second harmonic generation; azobenzene; adsorption; photoisomerization

INTRODUCTION

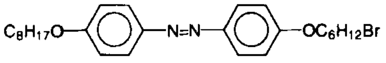
Azobenzenes having two alkoxy substituents at the 4- and 4'- positions are expected to afford large changes in second order molecular hyperpolarizabilities (β) due to photoisomerization; negligible in the *trans*-form ($\beta \sim 10^{-32}$ esu), while considerably large in the *cis*-form ($\beta \sim 10^{-30}$ esu) (scheme1) [1].



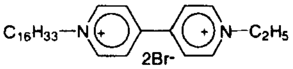
SCHEME 1 β–Values of dialkoxyazobenzene isomers

Recently, we reported in-situ second harmonic generation (SHG) responses from 4,4'-dialkoxyazobenzene derivatives adsorbed at the interface between an alkane solvent and a glass plate modified with a pyridinium compound [1-3]. It was also verified that molecular recognition at the interface was essential to increase the degree of noncentrosymmetric alignment of the *cis*-isomer, leading a large SHG response. Changing the viewpoint, the SHG technique is powerful to in-situ probe chemistry and/or physics of molecules noncentrosymmetrically aligned at the interface [4-6].

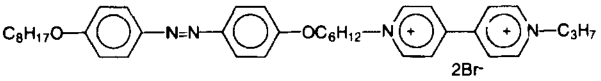
In this study, we report spectroscopic studies on SHG responses from *cis*-dialkoxyazobenzene entrapped at the viologen-modified glass/heptane interface, by comparing the results of nonlinked (AzoOR + ECV) and linked (Azo-V) molecular systems. Photochemical modulation of the SHG response was possible.



AzoOR



ECV



Azo-V

EXPERIMENTAL

A quartz glass plate (8 mm × 40 mm × 1 mm) was first treated with a KOH-saturated ethanol solution. Then the plate was immersed into a methanol solution of ECV (5×10^{-4} M) or a ethylacetate-methanol (95:5 V/V) solution of Azo-V (5×10^{-5} M) for 90 minutes to complete adsorption. After withdrawal, the glass plate was washed with heptane and dried in air.

The experimental geometry for SHG-photoisomerization measurements is shown in Figure1. In-situ SHG measurements were carried out by using fundamental light of a Nd:YAG laser (1064 nm, 5-7 ns, 10 Hz, ~20 mJ). The second harmonic (SH) signal was detected by the time-gated detection system. Photoisomerization of dialkoxyazobenzene was performed by using a high-pressure Hg lamp (500 W).

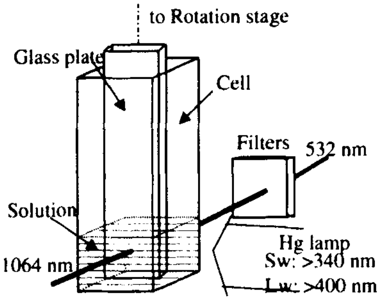


FIGURE 1 Experimental geometry for photoisomerization-SHG measuremenets.

RESULTS AND DISUCUSSION

Photoisomerzation of *trans* → *cis* or *cis* → *trans* was performed by ultraviolet (Sw: > 340 nm) or visible (Lw: > 400 nm) light from the Hg lamp. Figure 2 (a) shows spectral changes in AzoOR (2×10^{-4} M) in heptane. Before irradiation, AzoOR exists as the *trans*-form. The Sw-light irradiation results in a *trans*-to-*cis* isomer ratio of ~ 3:7 (*cis*-rich), while the subsequent Lw-irradiation leads to the isomer ratio of ~ 7:3 (*trans*-rich). Thermal *cis* → *trans* isomerization in the dark is considerably slow (Figure 2(b)), and thus its does not affect during the SHG measurements (several minutes).

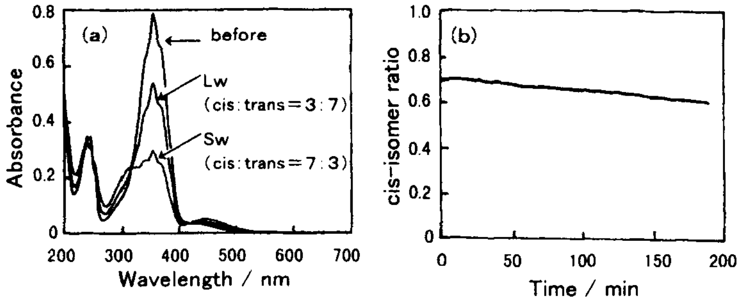


FIGURE 2 (a)Absorption spectra of AzoOR in heptane (2×10^{-4} M) before and after Lw- or Sw- irradiation; (b) Degradation of *cis*-isomer after ceasing Sw-irradiation.

Figure 3 shows angular dependencies of SH signals from the ECV-modified glass plate in heptane in the absence or the presence of AzoOR (2×10^{-4} M) at the *cis*-rich condition. The clear SH signal was observed only in the presence of both compound (ECV and AzoOR). The bare glass plate gave no appreciable SH signals even in the presence of AzoOR. These results show that some noncentrosymmeric assembling of the *cis*-isomer is formed at the interface by the interaction with ECV.

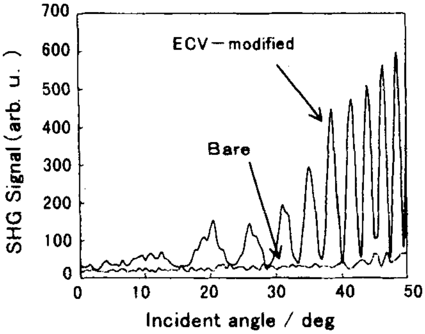


FIGURE 3 Angler dependencies of SH signals from ECV-modified and bare plates in a AzoOR-heptane solution (2×10^{-4} M)

As shown in Figure 4, the absorption spectra of the ECV-modified plate before and after SHG measurements were essentially identical;

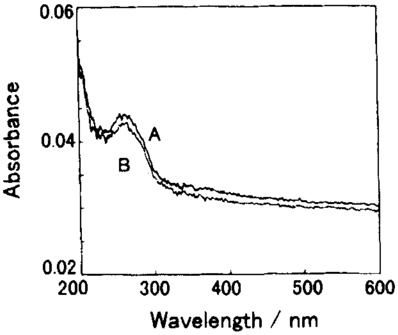


FIGURE 4 Absorption spectra of the ECV-modified glass plate in heptane before (A) and after (B) SHG measurements.

the fractional coverage was 9.2×10^{-11} mol/cm^2. Thus, ECV does not peel off and AzoOR does not deposit on the plate. Noncentrosymmetric assembling of the *cis*-isomer is achieved only at the ECV-modified glass/solution interface.

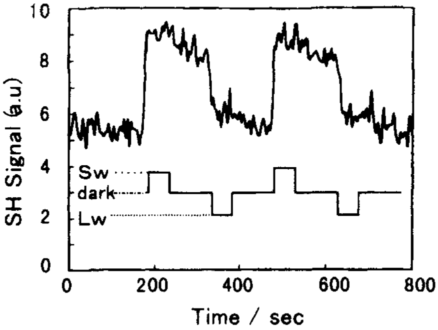


FIGURE 5 Variation of SH signals at fixed incident angle on photoisomeri-zation of Azo-V confined at the glass surface in heptane.

In the case of the Azo-V-modified plate, clear SHG responses were observed in heptane. Figure 5 shows changes in the SH signals at a fixed incident angle (~45°) during repeated Sw (1 min)-dark-Lw (1 min) irradiation cycles. Changes of SHG reposes were quite reproducible, indicating no peed-off of Azo-V from the glass surface and reproducible noncentrosymmetric assembling during repeated photoisomerization. Absorption spectra of the Azo-V-modified plate in heptane by Lw- and Sw- irradiation are shown in Figure 6; the spectra were quite reproducible and the isomer ratios were almost identical to the case of AzoOR in methanol.

In a previous study, partial irradiation experiments revealed the presence of adsorption/desorption equilibrium of dialkoxyazobenzene at the modified glass/alkane interface [1]. The present study also indicate that this equilibrium was seen only at the interface between the modified plate and the heptane solution. No appreciable interactions between them were seen in air.

Previously, we also reported that the SHG response from the *cis*-isomer was larger when the distance between two pyridinium moieties of a bispyridinium compound adsorbed at the glass surface was smaller [3]. Thus, it is also suggested that a 1:1 molecular interaction between the *cis*-isomer and ECV is responsible for noncentrosymmetric alignment of the *cis*-isomer, as schematically shown in Scheme 2.

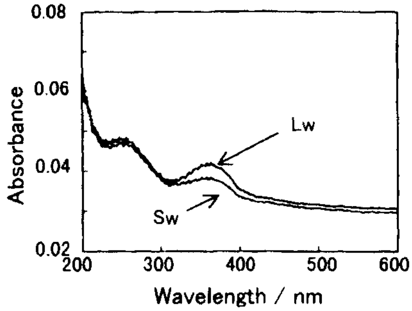
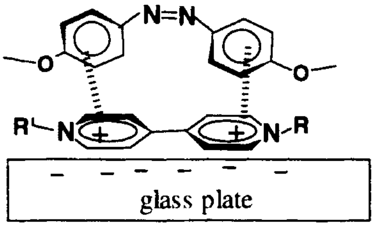


FIGURE 6 Absorption spectra of Azo-V-modified plate by Lw- and Sw- irradiation.



SCHEME 2 Proposed interaction.

The result of Figure 5 shows that the SH light can be modulated by photoisomerization. Use of pulsed laser lights for photoisomerization is fascinating as photochemical modulation of the and the work is in progress along this line.

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