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Adsorption Behaviors of Anionic Dyes in Alternately-Assembled Polyion-Dye Nonlinear Optical Films

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Total internal reflection spectroscopy has been applied to investigate adsorption behaviors of anionic dyes to a polyion layer in an aqueous solution. Three kinds of dyes with one, two, and three sulfonate groups were compared. The adsorption process was completed in a longer time and the equilibrium constant of the Langmuir isotherm became larger as the number of sulfonate group decreased. The deposition quantity of the dye was also in this order. Polarization measurements of optical second harmonic signals indicated that the average nonlinear polarization vectors were titled similarly in the three dye films.

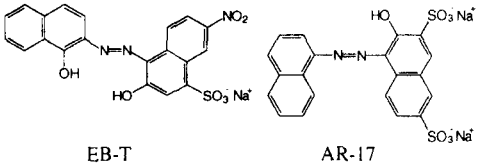
Key words : electrostatic adsorption, polyion-dye assembly, total reflection absorption, second harmonic generation, NLO films

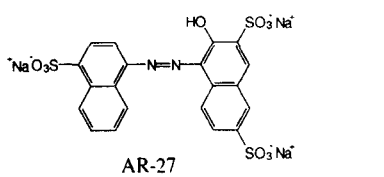
1. INTRODUCTION

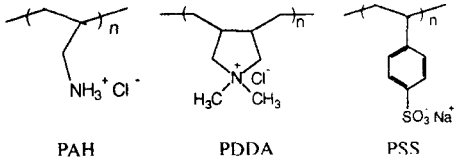
The development of ultrathin organic films with highly-efficient nonlinear optical (NLO) properties is one of the most promising subjects in optoelectronic devices. Various attempts have been made to design NLO films.

Recently, a novel method of preparing ultrathin organic films by alternate layer-by-layer electrostatic adsorption was reported [1-4]. Using this method, we first reported second harmonic generation (SHG) responses from the layer-by-layer films consisting of the combination of polycation and polyanion [5] or polycation and a low-molecular weight dye [6]. This method is advantageous in film fabrication, because it needs no sophisticated instrumentation and a large variety of water-soluble species can be used. However, detailed noncentrosymmetric adsorption mechanisms have not been studied yet.

In this paper, we in-situ observed adsorption behaviors of some SHG-active anionic dyes with different numbers of sulfonate group to a polyion layer in an aqueous solution, using the technique of total internal reflection absorption. The deposition behavior of the dye was also investigated by the SHG technique.







2. EXPERIMENTAL SECTION

All chemicals, poly(allylamine)hydrochloride (PAH, Aldrich, μ_w 50000-70000), poly(diallyldimethyl-ammonium chloride) (PMMA, Aldrich), poly(sodium styrenesulfonate) (PSS, Aldrich, μ_w 70000), eriochrome Black T (EB-T, Dojindo), Acid Red 17 (AR-17, Aldrich), and Acid Red 27 (AR-27, Aldrich) were used as received. Water was purified by a Milli-Q system (Millipore).

The experimental arrangement for total internal reflection absorption measurements is shown in Fig. 1.

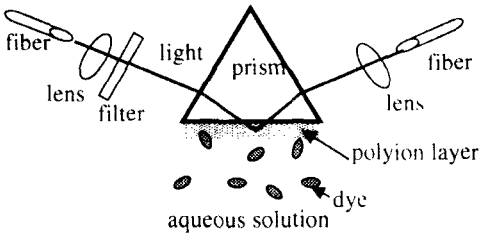


Fig. 1 Schematic illustration for total reflection absorption measurements at the polyion-solution interface.

The light from a halogen lamp (USHIO JCR 15V-150W) was introduced into an equilateral prism (SIGMA, SF18) at an incident angle of ~60°. The reflected light from the interface region of the prism surface and an aqueous dye solution was collected by a lens and an optical fiber, and was analyzed by a multichannel photodetector (UNION GIKEN MCPD-100).

The surface of the prism was treated with fuming nitric acid for 10 minutes and then with alkaline aqueous solution (1% KOH, 60% ethanol) for 20 minutes. One surface of the prism was dipped into an aqueous solution of PAH (1mg/ml) for 20 minutes, followed by rinsing with water and drying with nitrogen gas. Subsequent assembling of PSS (3 mg/ml, 20 minutes) and PAH or PDDA (1 mg/ml, 20 minutes) was carried out in the same procedure as above, to give a

$(PAH/PSS)_2(PDDA)$ five-layered polyion film (outermost layer : PDDA). The $(PAH/PSS)_2$ layer acted as a precurson film. This polyion film was in contact with the aqueous dye solution in a temperature-controlled cell (20 ℃). The temperature of the dye solution was also controlled at 20℃ beforehand. The time dependence of the reflection absorption change was followed after introducing the sample solution into the cell. The effect of dye concentration was investigated after 20 minutes from the introduction of the sample solution, when the adsorption had already reached constant.

The experimental setup for SHG measurements has been described previously [5, 6]. The p-(parallel to the incident plane) polarized fundamental light from a Nd:YAG laser (1064 nm, ~20 mJ, 7 ns, 10 Hz) irradiated the sample and the p-polarized component of the transmitted second harmonic light (I_{pp} : 532 nm) was detected. The $(PAH/PSS)_2(PDDA/dye)$ films were fabricated on the surfaces of a glass plate (40×13×1 mm) in a similar manner as described above.

3. RESULTS AND DISCUSSION

Figure 2 shows reflection absorbance changes as a function of time after introducing the dye solution into the cell. In the case of EB-T (a), the absorbance increased gradually and reached almost constant after 20 minutes. As to AR-17 (b) and AR-27 (c), on the other hand, absorbance changes were almost constant, indicating that the adsorption had already reached equilibrium before the commencement of absorption measurements. Thus, EB-T tends to adsorb to the PDDA layer much more slowly than the others.

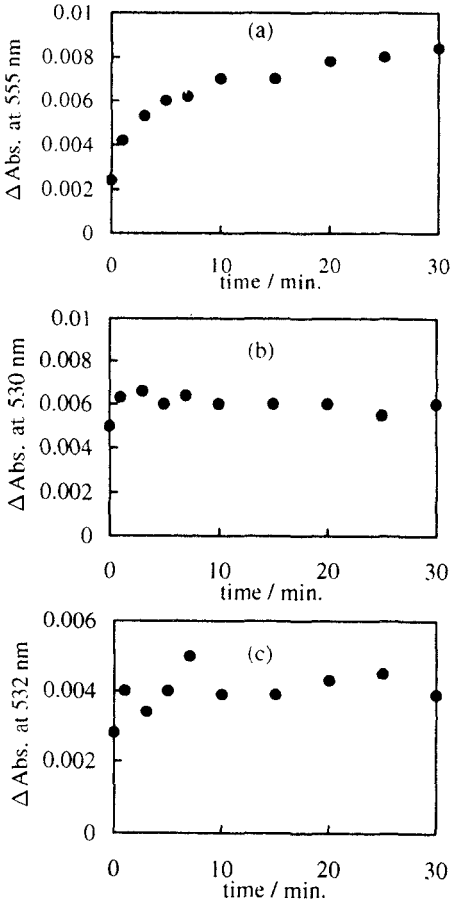


Fig. 2 Time dependences of reflection absorbance change (Δ Abs) at the interface between the $(PAH/PSS)_2(PDDA)$ layer and the dye solution, after introducing the dye solution (1×10^{-4} M) into the cell. Dyes : (a), EB-T ; (b), AR-17 ; (c), AR-27.

The relationships between the reflection absorbance change and the dye concentration are shown in Fig. 3.

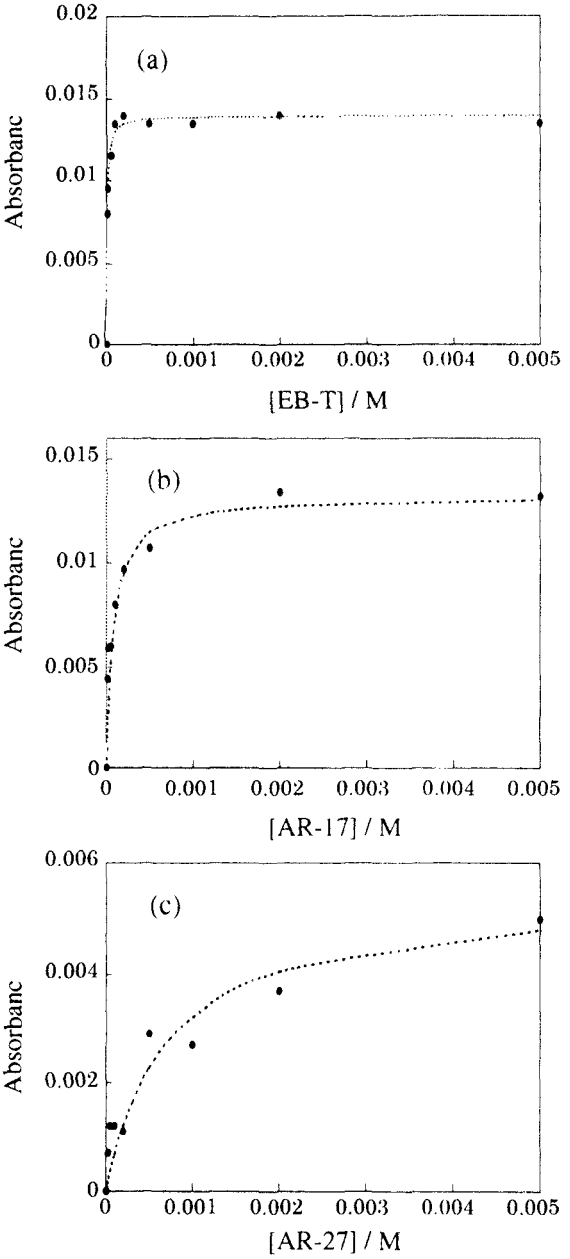


Fig. 3 Relationships between reflection absorbance change and dye concentration : (a), EB-T ; (b), AR-17 ; (c), AR-27.
Solid lines are the best fits to equation (1) for K values : (a), 1.3×10^5 M^{-1} ; (b), 1.3×10^4 M^{-1} ; (c), 1.4×10^2 M^{-1}.

Solid lines show best fits to the Langmuir isotherm.

$$\theta = \frac{KC}{1 + KC} \quad \cdots\cdots\cdots\cdots (1)$$

where θ is the fractional coverage, C is the dye concentration in solution, and K is the equilibrium constant : 1.3×10^{5} M^{-1} for EB-T (a), 1.3×10^{4} M^{-1} for AR-17 (b), 1.4×10^{2} M^{-1} for AR-27 (c) [7]. Clearly, the K value was in the order of EB-T > AR-17 > AR-27, inverse order of the number of sulfonate group. Probably, hydrophobic interactions between EB-T and PDDA assist the adsorption of EB-T.

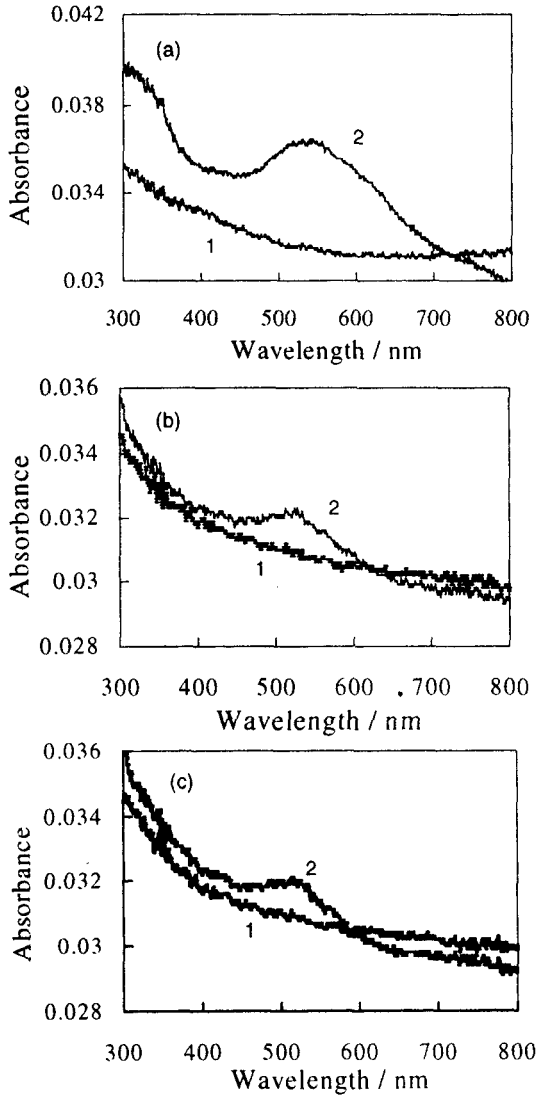


Fig. 4 Absorption spectra before (1) and after (2) deposition of dye on the $(PAH/PSS)_2(PDDA)$ film in air : (a), EB-T ; (b), AR-17 ; (c), AR-27.

In order to evaluate the deposited quantity of the dye, following experiments were carried out. The glass plate modified with the $(PAH/PSS)_2(PDDA)$ film was immersed into the aqueous dye solution (1×10^{-4} M) for 20 minutes. After withdrawal, the plate was rinsed with water for 1 minute and dried. Absorption spectral change before and after deposition of the dye is shown in Fig. 4. Fluctuation of baseline was unavoidable due to very low absorbance. Surface densities of the deposited dyes were calculated to be $\sim2\times10^{-10}$ mol/cm^2 for EB-T, $\sim4\times10^{-11}$ mol/cm^2 for AR-17, and $\sim 2\times10^{-11}$ mol/cm^2 for AR-27 [8], respectively; they were correlated with the corresponding K values (Fig. 3).

Angular dependences of I_{pp} from the $(PAH/PSS)_2(PDDA/dye)$ films are shown in Fig. 5.

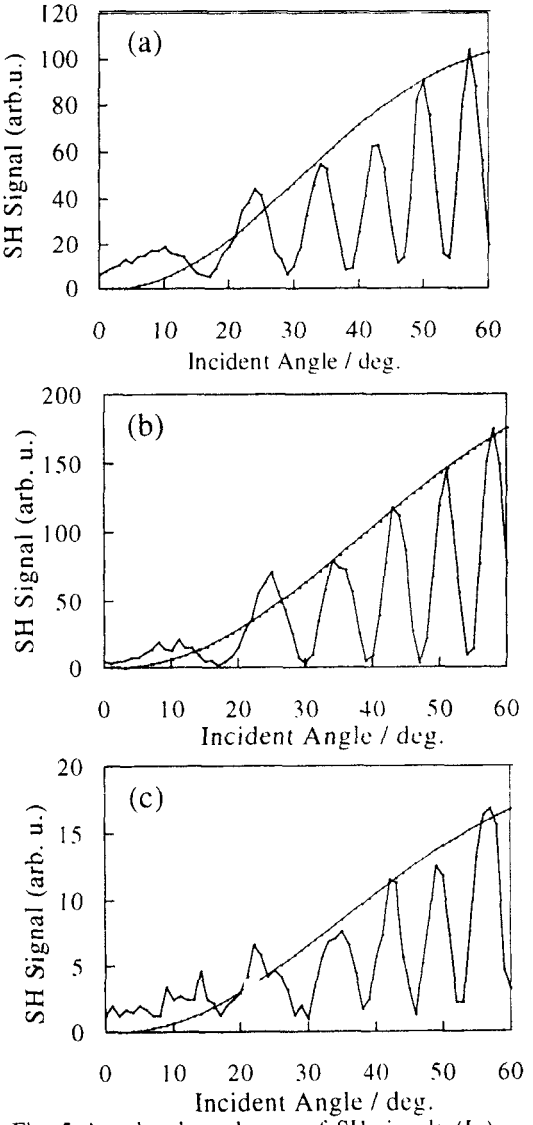


Fig. 5 Angular dependences of SH signals (I_{pp}) from $(PAH/PSS)_2(PDDA/dye)$ films. Dyes : (a), EB-T; (b), AR-17; (c), AR-27.
Solid lines show best fits to equation (2) for γ values : (a), 45°; (b), 42°; (c), 43°.

The interference fringe pattern of the signal due to the interference of SH waves from the both surfaces of the substrate is destructive, implying uniform quality of dye deposition. The signal profile could be fitted to the theoretical I_{pp} based on the projection model as:

$$I_{pp} = A\,(1.5\tan^2\gamma\sin\alpha\cos\alpha + \sin^3\alpha)^2 \quad \cdots\cdots\cdots (2)$$

where γ and α represent the average tilt angle of molecular hyperpolarizability tensor and the incident angle, respectively, and A is a proportionality constant [9]. Solid lines are the best fits to the equation (2), taking $\gamma = 45^\circ$ for EB-T, 42° for AR-17, and 43° for AR-27, respectively. Thus, the average directions of nonlinear polarization are similar in all films.

These results suggest that some noncentrosymmetric ordering of the dye molecules is achieved in the adsorption process, though its degree is still uncertain. The degree of noncentrosymmetric adsorption was higher for the molecular with higher hydpophobicity. Thus, this method is quite useful for fabricating organic NLO films. Studies on the thermal stability of the SHG response are underway [10].

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[7] Unfortunately, we could not determine the maximum θ value from Δ Abs, because fluctuation of optical configuration was unavoidable in the exchange of the polyion-modified prism.
[8] Surface densities of the chromophores were evaluated from molar absorptivities of dyes in water; 1.5×10^4 $M^{-1}cm^{-1}$ (537 nm) for EB-T, 2.1×10^4 $M^{-1}cm^{-1}$ for AR-17 (522 nm), and 2.7×10^4 $M^{-1}cm^{-1}$ for AR-27 (522 nm).
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