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## *Communications*

### Intercalation of *p*-Nitroaniline into Tetramethylammonium Saponite Film under Electric Field and Its Optical Second Harmonic Generation

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The smectite group of layered clay minerals (such as saponite and montmorillonite) consists of negatively charged silicate layers and readily exchangeable interlayer cations and possesses various attractive features of immobilizing photoactive organic species such as adsorptive properties, chemical and thermal stability, film-forming ability, etc.[1,2] Since the characteristics of the photoprocesses are sensitive to the environment where the photoactive species are adsorbed, various important information on the surface properties have been clarified.[3-5] One of the most important advances in this research field is the microscopic modification of the surface properties by co-intercalation of organic species such as water soluble polymers[6,7] and organoammonium ions.[8-15]

On the other hand, the application of nonlinear optical processes to photonics has led researchers to search for new nonlinear optical (NLO) materials.[16,17] For materials to exhibit second harmonic generation (SHG), a noncentrosymmetric arrangement of the NLO active groups is required. It means that the SHG properties can also be used as a probe to know the arrangements of dipoles. One approach is to align dipoles in organic polymers[18] and sol–gel-derived xerogels[19] by applying an external electric field. Recently, "electric-field-assisted chemical vapor deposition" has been reported to prepare polyazomethine head-to-tail conjugated polymers with SHG.[20] Although excellent optical qualities have been achieved, the noncentrosymmetric alignments of the dipoles induced by

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external electric field tend to randomize. The other approach is the use of self-assembled molecular aggregates such as LB films and inclusion compounds, in which both organic[21-23] (cyclodextrin, deoxycholic acid, etc.) and inorganic[24-26] (zeolite, etc.) hosts have been used. By using the anisotropic structure, noncentrosymmetric alignments of dipoles can be obtained. Processing these host-guest systems into films is a current topic in order to apply them for optical devices, sensors, etc.[27]

In this communication, we report a novel way to align a NLO chromophore using a tetramethylammonium (TMA) saponite film as a host matrix. Since the film is transparent in the visible region and possesses ordered microporous structure,[28] their applications for immobilizing organic compounds is of both scientific and practical significance. *p*-Nitroaniline (abbreviated as *p*-NA) was selected as the guest species, because it has high second-order molecular hyperpolarizability, and its size is just equivalent to the dimension of the micropore of the TMA saponite. To achieve noncentrosymmetric alignment of the dipoles, an electric field was applied during the intercalation of *p*-NA.

The TMA saponite was prepared by an ion exchange between synthetic Na saponite and an aqueous solution of TMA chloride.[15] The TMA saponite was dispersed in deionized water and casted on a quartz or glass substrate to form thin film.[28] For the infrared study, self-supporting films were prepared by casting a suspension on a Teflon plate. The X-ray diffraction pattern of the TMA saponite film shows the basal spacing of 14.3 Å, which is in agreement with that of the TMA saponite powder. Since the *d*(001) diffraction peak is intensified compared with that of the powder and higher order reflections have been observed, the film is thought to be composed of aggregated silicate particles with their *ab* planes parallel to the substrate. The interlayer tetramethylammonium ion provides the interconnected micropore in the interlayer space and some ionically neutral organic molecules can be incorporated into the micropore from vapor phase or solutions.[28]

Intercalation of *p*-NA into the TMA saponite film was carried out by exposing the TMA saponite film in *p*-NA vapor at 120 °C under reduced pressure. By the reaction with *p*-NA vapor for a few hours, the TMA saponite film became pale yellow. The absorption spectrum of the reaction product is shown in Figure 1b together with that of the TMA saponite film. Absorption bands due to $\pi$–$\pi^*$ transition and n–$\pi^*$ transition of *p*-NA appeared around 380 and 230 nm, respectively in the absorption spectrum of the reaction product. In the XRD pattern of the product, no diffraction peaks due to the *p*-NA crystal were observed and the basal spacing of the TMA saponite (1.43 nm) did not change by the reaction. Additionally, even after the washing with acetone or ethanol, the adsorbed *p*-NA remained in the film. These observations indicate that *p*-NA was incorporated into the TMA saponite film and the adsorbed *p*-NA molecules occupy the interlayer micropore of the TMA saponite. Judging from the size and shape of both *p*-NA molecule and the micropore of the TMA saponite, the direction of dipole of *p*-NA cannot be perpendicular to the *ab* plane of the silicate layer. The *p*-NA molecules are assumed to be lying in the *ab* plane with some inclinations.

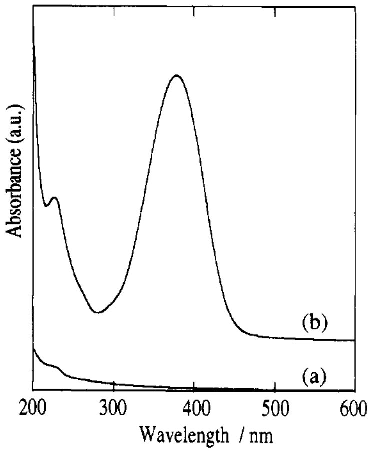

**Figure 1.** Absorption spectra of (a) the TMA saponite film and (b) the TMA saponite–*p*-NA intercalation compound.

If protonation of amino group occurred in the adsorption, n–$\pi^*$ transition should disappear in the absorption spectrum. Since the absorption band due to n–$\pi^*$ transition was observed in the absorption spectrum of the product (Figure 1), the adsorbed *p*-NA molecules were not protonated. The infrared spectrum of the self-supporting film after the reaction with *p*-NA showed absorption bands characteristic to *p*-NA, such as N–O symmetric stretching vibration of $NO_2$ (at 1331 cm$^{-1}$) and benzene ring frequency (at 1600 cm$^{-1}$).[29] The $\nu(NO_2)$ absorption band for a chloroform solution of *p*-NA appeared at 1335 cm$^{-1}$ which is shifted toward lower wavelength region than that (1338 cm$^{-1}$) of a carbon tetrachloride solution, and the shift has been ascribed to hydrogen bonding.[30] Taking the geometry of the TMA saponite into consideration, the $NO_2$ groups of the intercalated *p*-NA molecules are thought to be hydrogen bonded with $NH_2$ groups of adjacent molecules or TMA ions.

In our separate work on the photochemical hole burning of the TMA saponite–1,4-dihydroxyanthraquinone intercalation compound, we have reported that 1,4-dihydroxyanthraquinone was intercalated into the interlayer micropore of the TMA saponite by the solid–liquid reaction between the TMA saponite powder and an acetone solution of 1,4-dihydroxyanthraquinone. The solid–gas reactions reported here should be a better way for the incorporation because the quality of the film did not degrade after the reactions and the operation is simple. Incorporation of *N*-salicylideneaniline, *p*-aminoazobenzene, etc., into the interlayer space of the TMA saponite film by the solid–gas reactions has also succeeded, and the results will be reported subsequently.

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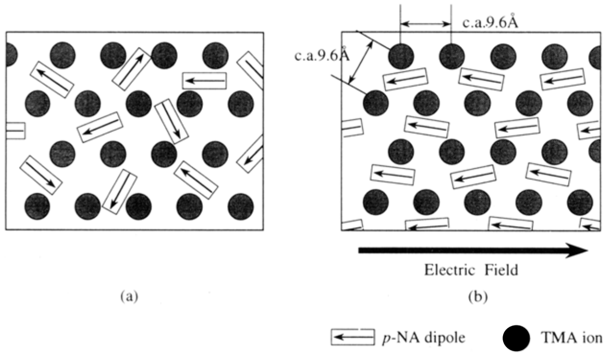

**Figure 2.** Schematic structure of the TMA saponite–*p*-NA intercalation compounds (a) without and (b) with an electric field during intercalation.

An Nd:YAG laser was used for the SHG experiment. No apparent SHG was observed for the TMA saponite–*p*-NA intercalation compound, suggesting that the direction of the dipoles of the adsorbed *p*-NA molecules were thought to be randomly distributed and the dipoles are macroscopically centrosymmetric. Since the direction of the dipoles is assumed to be in the *ab* plane of the silicate layers from the geometrical consideration mentioned above, the random distribution of the direction of the dipoles (schematically shown in Figure 2a) must be assumed.

In the present system, the *ab* planes of the silicate sheets are oriented parallel to the substrate as evidenced from the X-ray diffraction pattern of the film.[28] This indicates that the micropore of the TMA saponite are interconnected within the direction parallel to the substrate. To align dipoles in a direction within the micropore of the TMA-saponite, an external electric field was applied during the intercalation of *p*-NA. Slit type chromium electrodes with a 0.2-mm gap are deposited on the TMA saponite film and a dc electric field (10 kV cm$^{-1}$) was applied during the intercalation of *p*-NA. (The geometry of the sample and electrode is shown in Figure 3.) After the sample was cooled to room temperature, the electric field was removed and the SHG experiment was carried out. The compound prepared under the electric field exhibited SHG with the intensity of $10^5$ order higher than that for the compound prepared without electric field. This indicates that the applied electric field caused the alignment of *p*-NA dipoles with noncentrosymmetry in the interlayer space of the TMA saponite. The expected orientation of the dipoles is schematically shown in Figure 2b.

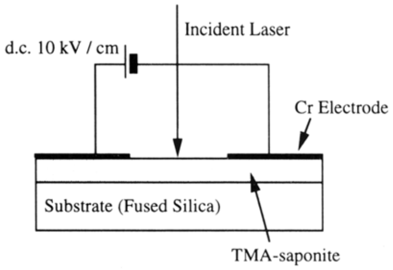

**Figure 3.** Schematic representation of experimental setup for the intercalation under electric field.

This is the first report on orientational control of organic species in inclusion compound by external signal. Because of the matching of the size and geometry of the TMA saponite and those of *p*-NA, the stability of the SHG should be different from those of conventional poled polymers. Moreover, the relaxation in the SHG activity as a function of time and temperature can also be applied as a measure of the dynamics of adsorbed species. The studies on the stability of the SHG activity and the optimization of reaction conditions (i.e., the intensity of the applied electric field and the loading amount of *p*-NA) are now underway and will be reported subsequently.

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