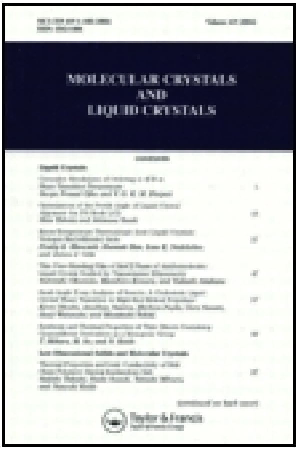

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Second-Order Nonlinear Optical Properties of the Hybrid-Film of a Clay and a Chiral Metal Complex

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Second-harmonic generation (SHG) properties of the hybrid-films of a clay and [Δ-Ru (4,7-diphenyl-1,10-phenanthroline)$_3$](ClO_4)$_2$ (Δ-Ru(dpp)$_3$), which was found to be stable enough over a very long time, were studied. The ratio of the SHG signal intensity between Z- and Y-Type films of Δ-Ru(dpp)$_3$ has been compared. Furthermore, the SHG coefficient d_{33} at 1.06 μm is determined as 30 pm/V for the Y-Type hybrid-film of Δ-Ru(dpp)$_3$.

Keywords: nonlinear optics; second-harmonic generation; SHG; hybrid-film; clay; metal complex

INTRODUCTION

Organometallic compounds have been considered to possess a large nonlinear optical coefficient owing to a metal-to-ligand and ligand-to-metal charge transfer (MLCT and LMCT) transition [1]. In addition, since organometallic compounds have a variable metal center (d electron, oxidation state, geometry and so forth) which is not available for conventional organic molecules, it is expected that those exhibit not only large optical nonlinearity but also several kinds of interesting features with respect to electronic- and magnetic properties and so forth. Therefore, the study of organometallic compounds for a nonlinear-optical (NLO) material is currently of great technological and scientific interest [2].

In this study, we have undertaken an investigation of second-order NLO properties of the hybrid-film composed of a clay and a metal complex. Second-order NLO phenomena are observed only when the component chromophores are aligned in a noncentrosymmetric array. However, organic and organometallic compounds have a tendency to crystallize in a centrosymmetric array in most cases. Therefore, a means of imposing a noncentrosymmetric structure on those compounds is needed. The Langmuir Blodgett (LB) technique is one of the various methods that can implement a noncentrosymmetric structure. However, for LB films, a few problems, which include poor thermal and mechanical stability, and poor optical quality, are often encountered [3]. We have succeeded in making a "stable" LB film by hybridizing a clay and a metal complex. Here a clay is chosen as a component reinforcing a film structure because it consists of two-dimensional ultra-thin layers (1 nm thick). So, second-harmonic generation (SHG) properties of the resulting hybrid-films were investigated. As a result, clear SHG responses have been observed.

SAMPLE PREPARATION

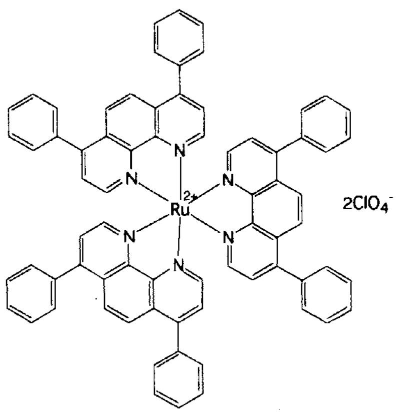

FIGURE 1. Chemical Formula of $[Ru(dpp)_3](ClO_4)_2$

A monolayer of [Δ-Ru(4,7-diphenyl-1,10-phenanthroline)$_3$](ClO_4)$_2$ (Δ-Ru(dpp)$_3$; Figure 1.) was formed onto an aqueous suspension of a clay. A single clay layer that was charged negatively was thought to attach the positively charged monolayer to form a clay-metal complex hybrid-film (Figure 2.). The Z-Type hybrid-films were prepared by the horizontal lifting method. On the other hand, the Y-Type hybrid-films were prepared by the vertical dipping method. The deposition of the hybrid-film on a fused silica substrate was achieved at a pressure of 15 mN/m. The procedure was made only one time for both cases.

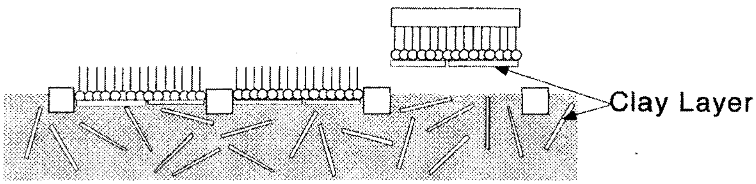

FIGURE 2. Schematic representation of the deposition of the hybrid-film of a clay and metal-complex by the horizontal lifting method.

OPTICAL EXPERIMENTS

The spectrum of UV-Vis-NIR on the substrate was measured by a JASCO Ubest-30 spectrophotometer. SHG measurements were made by using a pulsed beam from a Q-switched Nd-YAG laser (Quanta-Ray, Model DCR-2; 20Hz), operating at a wavelength of 1.064 μm with a pulse duration of 8 nsec and an energy of 2 mJ, was used for excitation.

RESULTS AND DISCUSSION

The absorption spectrum taken for the Y-Type hybrid-film of a synthesized saponite and Δ-Ru(dpp)$_3$ is shown in Figure 3. The result reveals that the wavelength of the second-harmonic wave (532 mm) is located at the tail of the charge-transfer absorption band. Consequently, weak resonant enhancement of the signal intensity of the second-harmonic generation (SHG) should be expected.

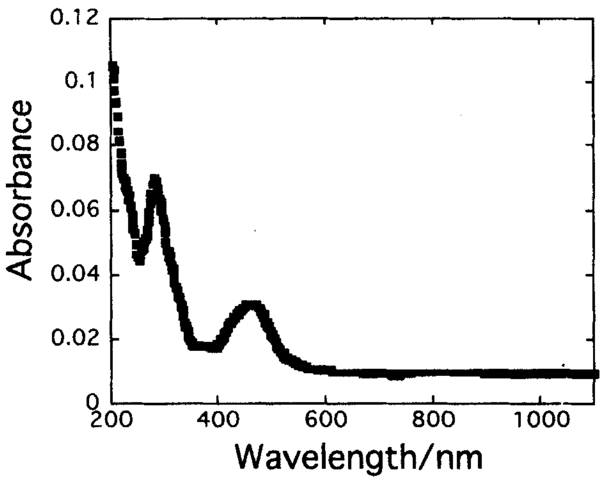

FIGURE 3. Absorption spectrum taken for the Y-Type hybrid-film of a synthesized saponite and Δ-Ru(dpp)$_3$.

The interference pattern for the Y-Type hybrid-film of the synthesized saponite and Δ-Ru(dpp)$_3$ is shown in Figure 4. Clear fringes of the SHG signal have been observed. The signal intensity observed for the film was four times as large as that of the Z-Type hybrid-film. In the case of the sample made by the vertical dipping method, there are two films, each being on both sides of the substrate. Therefore, the sample thickness of the Y-Type hybrid-film is two times as large as that of the Z-Type hybrid-film. Considering that, in case of very thin film, the SHG signal intensity is known to be in proportion to the square of the sample thickness, the relative magnitude of the SHG signal intensity is quite reasonable. Therefore, it is evident that the observed SHG signal is generated from the hybrid films.

The fringe pattern shown in Figure 4 has been analyzed in a way similar to the case of phenylhydrazone dyes [4]. As a result, the magnitude of d_{33} for the present film is estimated to be 30 pm/V by comparing the intensity to that of the Maker-Fringe due to d_{11} observed for a reference crystal of quartz; the magnitude of 0.50 pm/V was adopted for d_{11} of quartz crystal [5].

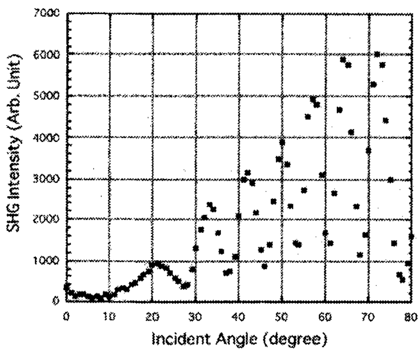

FIGURE 4. Angular dependence of SH signals from a $[Ru(dpp)_3]^{2+}$/ synthesized saponite hybrid film deposited at 15 mN/m.

In order to examine a change of the SHG signal intensity over a span of time, we have made the SHG measurements one-week and half-month after the film preparation. As a result, no apparent change of signal intensity with the passage of time has been recognized. This fact indicates that the present hybrid film is stable enough to support the validity of the SHG characteristics described thus far.

CONCLUDING REMARK

We have demonstrated that a SHG measurement on Δ-Ru(dpp)$_3$, a typical example of organometallic compounds, which are not necessarily easy to do, can be successfully made by utilizing the hybrid films. The results show that the present hybrid films are "stable enough" to investigate their SHG characteristics. Thus, it is concluded that the use of the hybrid LB films is very promising for the study of NLO properties for a number of metal complexes. It is remarked, however, that some fundamental aspects, such as the SHG signal intensity dependence on the concentration of the aqueous suspension of a clay, would be needed to be clarified. The experiments are now in progress.

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