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Optical Second Harmonic Generation from Ultrathin Polymer Films Impregnated with Ruthenium Polypyridine Complexes[1)]

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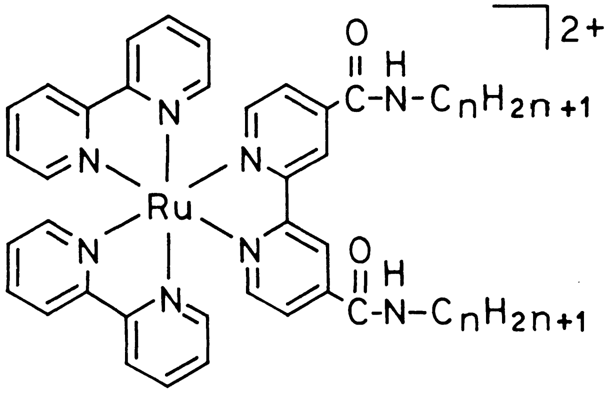
Second–harmonic–generation (SHG) was clearly observed with ultrathin poly(vinyl chloride) films (ca. 25 nm), impregnated with amphiphilic ruthenium tris(2,2'–bipyridine) complexes. On the basis of SHG intensity from multilayered assembly of the thin film, the laser–induced polarization of the second harmonic wave was concluded to have a big component in perpendicular direction with respect to the film surface.

Optical second harmonic generation (SHG) has frequently been observed, when a laser beam passes through medium consisting of noncentrosymmetric array of molecules with a low–lying charge–transfer resonance state.[2)] The so–called two–level model has been used to explain the observation as due to mixing of the charge–transfer state with the ground state through the action of the electric field of laser beam. In agreement with this explanation, aromatic compounds with donor– and acceptor groups at the conjugating sites have been known as useful material for SHG. On the basis of the two–level model, one should also expect that metal–to–ligand charge–transfer (MLCT) states of metal complexes will contribute to SHG. The best examples of metal complexes with MLCT transition is ruthenium(II) tris(2,2'–bipyridine). In fact, the present authors have discovered that SHG can be easily induced by the use of the following amphiphilic derivatives incorporated in LB film.[3)]

In addition, the amphiphilic ruthenium complex in LB film provided an optical means of modulating SHG for the first time. The intensity of SHG was reduced by 40% on irradiation of the metal complex with 355 nm light.[4)] The present paper describes a novel means of preparing ultrathin polymer–film, which incorporates the amphiphilic ruthenium complexes to afford SHG–active material.



RuC$_n$B

The ultrathin polymer–films were prepared by the use of a recipe, as provided by Kajiyama and his associates.[5)] Poly(vinyl chloride) and the amphiphilic ruthenium complex were dissolved into toluene–THF mixed solvents

(1:1, v/v). The poly(vinyl chloride) (degree of polymerization, 1100) was used as purchased from Wako Pure Chemicals. The solution was prepared by dissolving 0.1 g of poly(vinyl chloride) into 2 ml of the toluene–THF mixed solvent. The solution was carefully spread over pure water surface in a Teflon dish by the use of a microsyringe (100 μl). The ultrathin film with a circular shape (8 –10 cm in diameter) quickly appeared on the water surface as the solvent was evaporated. A square plastic frame (3 cm x 4 cm), as prepared with a polyester sheet (0.1 mm thick), was put on the floating film. A self-supporting, ultrathin film was obtained by picking up the plastic frame with a pair of tweezers. Thickness of this ruthenium-impregnated, ultrathin film was estimated to be ca. 25 nm by weighing the sample with a known area. The ultrathin film on the plastic frame was irradiated by the fundamental wave (1064 nm, 10 ns, 100 mJ/cm^2) of a Nd–YAG laser in a setup as described in a previous paper.$^{3)}$ The light emission from the film was detected by a photomultiplier, after passing through two IR-filters and a monochrometer. The time dependence of the emitted light was recorded with a storage scope. The signals were accumulated 10 times in each experiment and the peak-heights of the signals under various conditions were compared in the following experiments.

The intensity of SHG smoothly increased with the incident angle (θ, as defined in the inset of Fig. 1) of the laser beam. This is the same results as observed with the LB film of the amphiphilic ruthenium complex deposited on only one-side of a glass substrate.$^{3)}$ For a given incident angle, the second harmonic light (SHL) intensity became stronger with the increase of ruthenium complex concentration in the toluene–THF mixed solution up to ca. 2 mM. Additional increment was hardly observed with the 4 mM ruthenium solution as shown in Fig. 1.

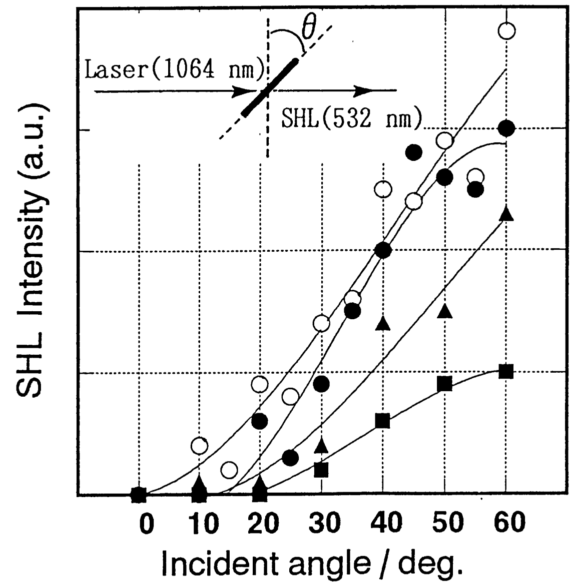


Fig. 1. Effects of ruthenium complex concentration on the SHL intensity: 0.5 (■), 1.0 (▲), 2.0 (●), and 4.0 mM (○) of RuC16B in the toluene–THF mixed solution.

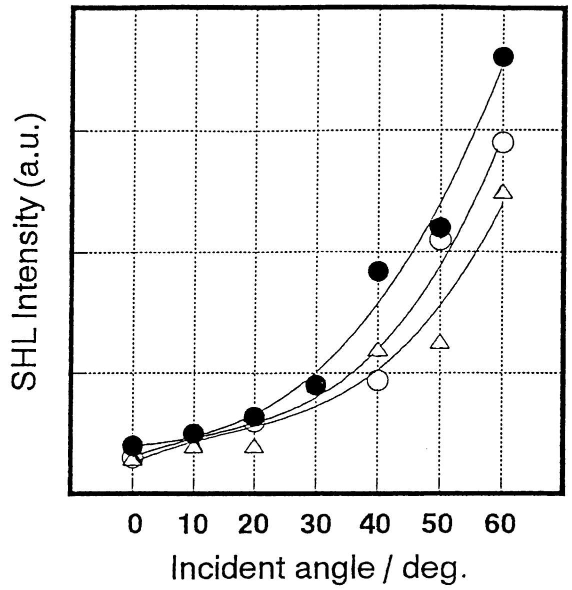


Fig. 2. Effects of alkylchain length on the SHL intensity: RuC12B (○), RuC16B (●), and RuC18B (△).

Contact angles of water-droplets indicate that bottom side of the ultrathin film (i.e. the side of polymer-water interface in the film preparation process) is hydrophilic in the investigated concentration range of the ruthenium complex. The opposite side of the film (i.e. the side of air-polymer interface in the film preparation), on the other hand, showed water-repelling properties until the ruthenium concentration reached 4 mM, where the contact angle started to decrease. On the basis of these observation, it is suggested that amphiphilic ruthenium complexes are preferentially concentrated to the bottom side of the film. The highly hydrophilic ruthenium trisbipyridine head group is most-likely exposed to the polymer-water interface.

Effects of alkyl chain-length on the SHL intensity are shown in Fig. 2. The measurements were carried out with the ultrathin films as prepared from the toluene-THF solutions containing 2 mM ruthenium complexes. In the case of these three alkyl groups with moderately long chain length (n=12, 16, and 18), no appreciable difference was observed. As to the alkyl groups with shorter chain length (n=2 and 6), no ultrathin film was obtained in the present experiment because the ruthenium complexes

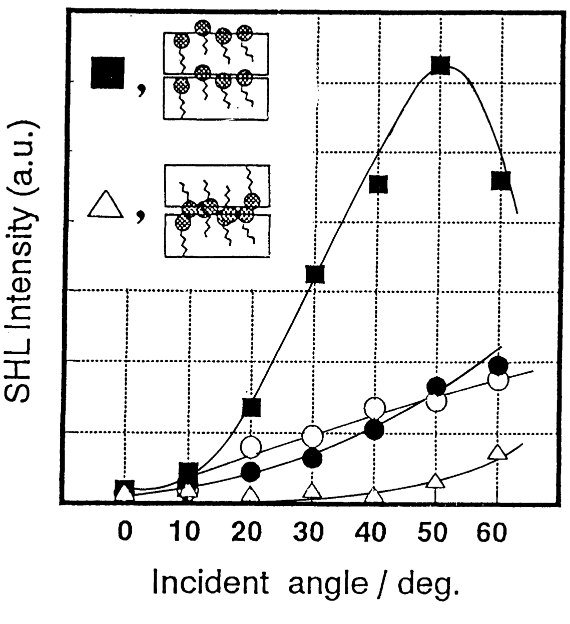


Fig. 3. Comparison of SHL intensity from laminated films in two different orientations: sitting-on-top type (■) and head-to-head type (△). The SHL intensity from two separately prepared, single layer films is also shown as the reference (○ and ●). The film orientations are illustrated in the inset of the figure. Hydrophilic side of the membrane is schematically shown by inscribing the symbol of amphiphilic ruthenium complex RuC16B (●〰〰: 2 mM).

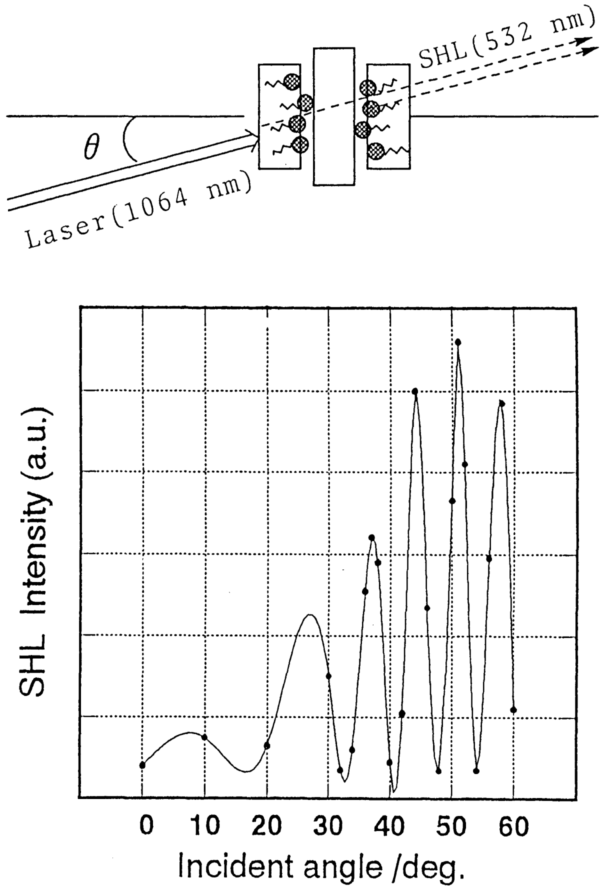


Fig. 4. Fringe patterns of SHL from the two films separated by a glass substrate (0.8 mm thick). The films were prepared by the use of RuC16B (2 mM in the toluene-THF solutions).

could not be dissolved into the toluene–THF mixed solvent. In order to obtain the ruthenium–complex–impregnated ultrathin film, it is apparent that one should counterbalance the hydrophilicity of the ruthenium moiety by the use of extremely hydrophobic alkyl chains in the same molecule.

Asymmetric property of the ultrathin film was revealed by comparing the SHL intensity as observed with double layers of the film in two different orientations (Fig. 3). Essentially identical SHL intensity was observed with two separately prepared, single layers of the ultrathin films (open- and filled circles). More than two–fold increase in the SHL intensity was observed, when the two layers of ultrathin film were superimposed in the same orientation (i.e. sitting–on–top type laminate as shown by filled squares in Fig. 3). In the case of head–to–head type laminate (open triangles), on the other hand, the SHL intensity became negligible in comparison with that for the single layer (open- and filled circles). Thus, it is clearly demonstrated that the laser–induced polarization of the second harmonic wave has a big component in perpendicular direction with respect to the ultrathin–film surface. The origin of this polarization should be ascribed to alignment of the ruthenium complexes at the bottom surface as schematically shown in Fig. 3. The upper surface of the ultrathin film is apparently inactive to SHG. The ruthenium complexes may be randomly oriented, if they exist any at the upper surface.

Fringe patterns due to interference were observed, when the incident angle dependence of the SHG intensity was examined with the two films separated by a glass substrate (Fig. 4). This is exactly the same as observed with the ruthenium complexes in LB films at the both sides of a glass substrate.[3] Then the observation may be taken as another evidence to demonstrate that the alignment of the amphiphilic ruthenium complexes at the bottom of the single ultrathin film is capable enough to provide a SHG–active surface.

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References

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