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Second Harmonic Generation by the Use of Metal to Ligand Charge-Transfer Transition of Ruthenium(II)-Bipyridine Metal Complex in Langmuir-Blodgett Film[1)]

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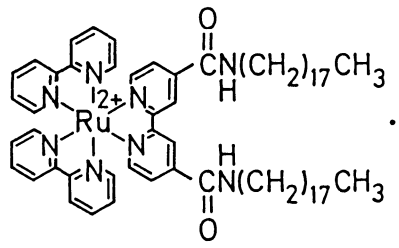
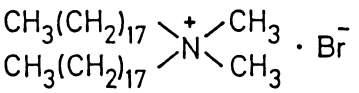
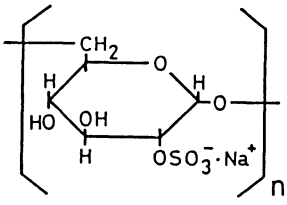
An alternate Y type LB multilayer capable of SHG was prepared by the use of an amphiphilic ruthenium(II) tris(2,2'-bipyridine) complex. The large angular dependence of the second harmonic light intensity and the electronic absorption of the multilayer indicated that the SHG was due to MLCT transition of the ruthenium complex.

By virtue of the large polarizability of π-electron systems, organic compounds have been expected to afford better materials for the second harmonic generation (SHG) in comparison with inorganic materials. Particular emphasis has been laid on the nonlinear optical properties of organic compounds containing highly conjugated π-electron systems with donor and acceptor moieties. The typical examples are benzene-, stilbene-, and azobenzene derivatives with electron donors and acceptors.[2)] In the case of these examples, the contribution of electronic transitions with charge-transfer character has been believed to be in favor of SHG. One would analogously expect that the metal to ligand charge-transfer transition (abbreviated to MLCT) in metal complexes may also be useful for SHG. However only few reports on SHG in metal-organic compounds are available so far.[3)] Ruthenium(II) tris (2,2'-bipyridine) complexes are well known to be associated with the MLCT electronic transition and the photochemical properties have been thoroughly investigated. In the present experiment, amide groups were introduced on one of the three bipyridine ligands of the ruthenium complex to increase the

RuC18B  $\cdot 2ClO_4^-$

2C18NB 

Dex  $n = 5 \times 10^4$

vectorial properties of the MLCT, and the metal complex was incorporated into LB film in order to obtain noncentrosymmetric alighnment of the molecules as required for SHG.

The LB film was an alternate Y type multilayer film, which was prepared by repeating alternate deposition of a dye layer and a matrix layer. An ammonium amphiphiles (2C18NB) was used to prepare the matrix layer, while dye layer was consisted of RuC18B and 2C18NB in 1:4 molar ratio. Both the dye- and matrix layers contained Dex poly anion to stabilize the films, which were deposited at 25 ℃ under a surface pressure of 20 mN/m on a slide glass treated with a silane coupling agent. The film assembly was irradiated with Nd^{3+}-YAG laser pulses (1064nm, 10ns, 100mJ/cm^2) and the luminescence from the sample was detected by a photomultiplier tube, after passing through two filters (a $CuSO_4$ aqueous solution and IRA-25S glass filters) and a monochromator.

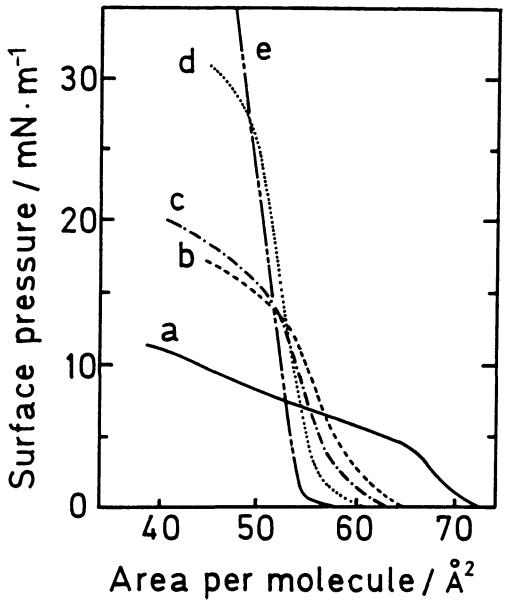


Fig. 1. Pressure-area isotherm for RuC18B-2C18NB monolayer on aq. Dex (0.25mM) at 14 ℃ in the following molar ratios (RuC18B:2C18NB) : (a) 1:0 (b) 2:3 (c) 3:7 (d) 1:4 and (e) 0:1.

The surface pressure-molecular area isotherms for RuC18B-2C18NB systems developed on an aqueous Dex solution (0.25 mM) subphase are shown in Fig. 1. The estimated molecular area for RuC18B in the monolayer is about 70 Å^2. The monolayer of RuC18B alone was not so stable and collapsed above 5 mN/m, while a stable condensed monolayer was obtained by adding appropriate amounts of 2C18NB. The best LB film was obtained by the use of RuC18B-2C18NB mixture in 1:4 molar ratio.

The temporal profile of SHG from the sample with 72 layers of alternate LB films on each side of the substrate is shown in Fig. 2. The signal width was the same as that of incident laser pulse. The signal is attributed to SHG, since it was not emitted from the usual, centrosymmetric Y type LB film of RuC18B-2C18NB composite in 1:4 molar ratio.

The second harmonic intensity was strongly affected by the variation of incident angle of the laser beam, and a fringe pattern was obtained by the use of LB films deposited on both faces of the substrate (Fig. 3(a)). As to the LB films deposited on only one side of the substrate, the fringe pattern disappeared and the harmonic light intensity rapidly increased with the incident angle (Fig. 3(b)). These results are in good agreement with the reported features of SHG from LB monolayer of stilbazolium and phenylhydrazone dyes on a quartz plate.[4] Since the coherent length of second harmonic is much larger than the film thickness, it is strongly suggested that the pattern in Fig. 3(a) is not a Maker fringe, but an interference fringe which arises from dephasing of the two second harmonic lights generated at the both faces of the substrate.[4] The phase difference between the harmonic lights are mainly introduced by the dispersion of the refractive indices

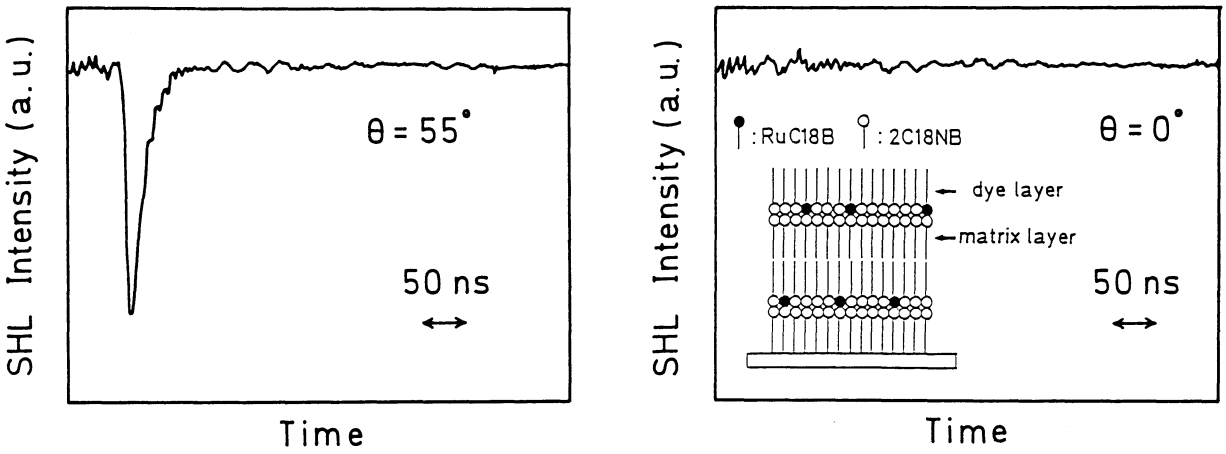


Fig. 2. Temporal profiles of second harmonic light (SHL) from the alternate LB multilayer (72 layers on each side of the substrate) of RuC18B-2C18NB (1:4 molar ratio) with two incident angles θ.

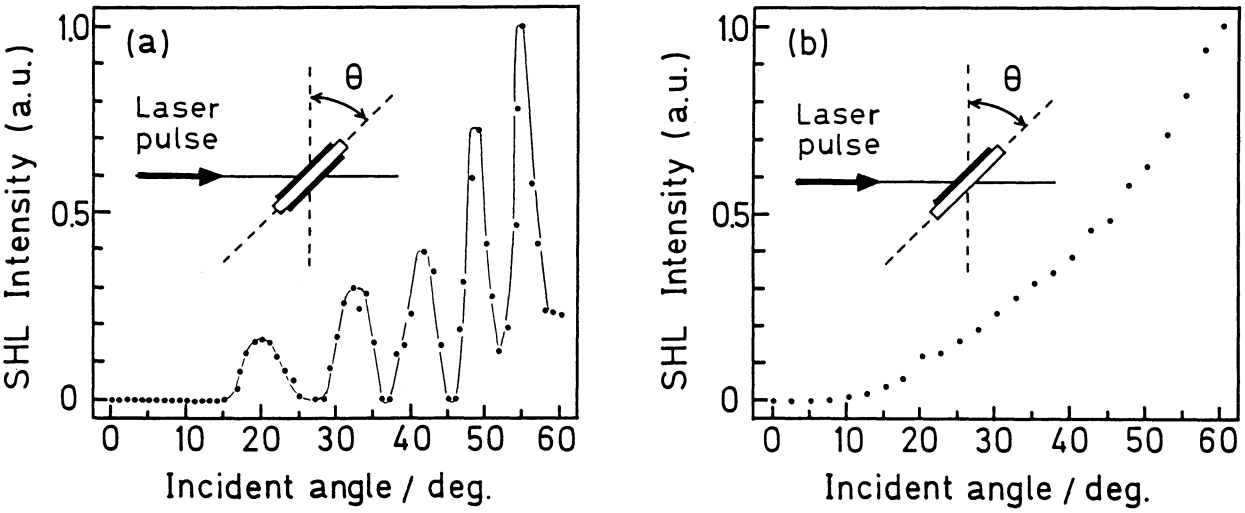


Fig. 3. Angular dependence of the second harmonic light (SHL) intensity from RuC18B-2C18NB LB film (a) on both faces and (b) on one face of the substrate.

at the fundamental and harmonic waves in the substrate.

Since second harmonic light intensity rapidly increased with the incident angle, one would anticipate that the sum of the transition dipole moment responsible for SHG lies in perpendicular direction with respect to the film plane. In order to examine the transition dipole moment of ruthenium complex, the absorption spectra of RuC18B-2C18NB alternate LB film was measured by the use of the polarized lights. The angular dependence of absorption spectra as obtained with p-polarized light is shown in Fig. 4. On the increase of the incident angle of p-polarized light, the absorbance at 480 nm increased more rapidly than at 450 nm. It is well established that the MLCT transition in ruthenium(II) tris(2,2'-bipyridine) complex is located at 450 nm.[5] The absorption band at 480 nm may correspondingly be assigned to MLCT transition to 2,2'-bipyridine moiety attached

with amide group.[6] Then, one may suggest that the above described SHG is due to the presence of MLCT transition located at 480 nm, and the transition dipole moment is lifted off to a large extent from the substrate plane.

The second harmonic light intensity of the above described RuC18B-2C18NB (1:4 molar ratio) LB films (72 layers on each side of the substrate) was verified to be comparable to that of 1-methyl-4-(4-(N-octadecyl-N-methylamino)styryl)-pyridinium iodide (abbreviated to C18AStz)-2C18NB(2:3 molar ratio) LB film (monolayer on each side). Since the reported second order hyper-polarizability (β) for C18AStz is about 500 x 10^{-30} esu, [7,8] one can estimate the corresponding β-value for RuC18B. On the basis of the experimentally evaluated molecular area for RuC18B (70 $Å^2$) and C18AStz (30 $Å^2$), the estimated β-value for RuC18B is about 70 x 10^{-30} esu under an assumption that the orientation factor for RuC18B and C18AStz is almost the same. It should be emphasized that the β-value is comparable to that for 2-methyl-4-nitroaniline (45 x 10^{-30} esu).[9]

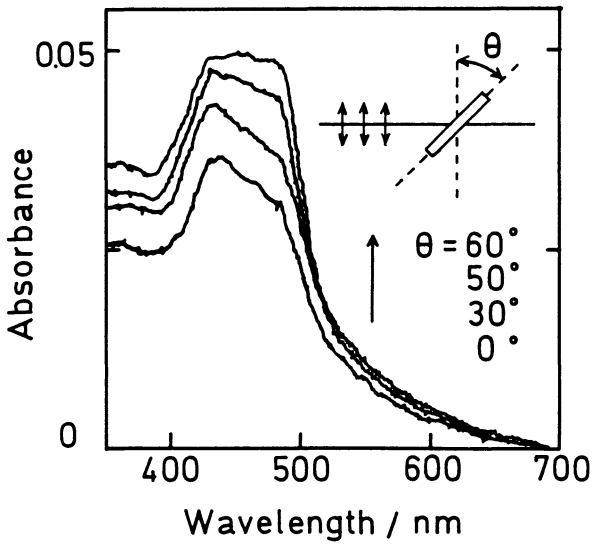


Fig. 4. Effects of incident angle of p-polarized light on the absorption spectra of RuC18B-2C18NB (1:4) alternate LB film.

In conclusion, a ruthenium(II) tris(bipyridine) derivative was successfully used to prove that MLCT transition in metal complex is extremely useful for SHG.

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