CHEMISTRY LETTERS, pp. 937-940, 1994.

In-Situ Observation of Second Harmonic Lights from Amphiphilic Ruthenium (II) Tris(2,2'-bipyridine) Complex at Glass/Liquid Interface

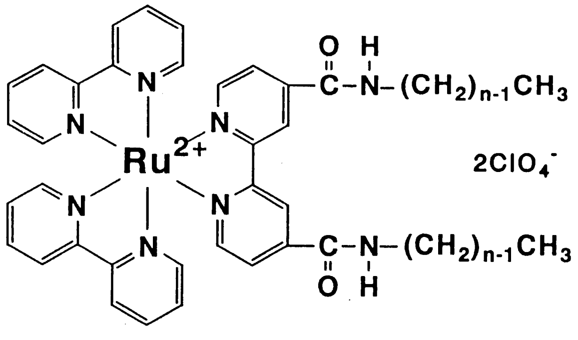
Sunao YAMADA, Yasuhiro YAMADA, Takashi NAKANO, and Taku MATSUO*
Department of Chemical Science and Tecnology, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

Interfacial second harmonic generation (SHG) from amphiphilic ruthenium(II)-tris(2,2'-bipyridine) complex (RuC12B) was clearly observed with an alkaline-treated glass substrate in a RuC12B - ethylacetate solution, but not with an octadecylsilyl (ODS)-derivatized glass substrate. Interference fringe patterns due to SHG strongly indicate that RuC12B is adsorbed at the alkaline-treated glass surfaces, with its head group pointing toward the glass surfaces.

Despite the basic importance and widespread interest in molecular adsorption at liquid/solid interfaces, in-situ probing of the phenomena has not been succesfully carried out by conventional spectroscopic techniques. A basic problem associated with spectroscopic studies at the interfaces is difficulty in discriminating surface species from those in bulk solution. Optical second harmonic generation (SHG) is inherently surface-sensitive, because SHG occurs only at noncentrosymmetric media. This technique has been proved useful in studies of physicochemical dynamics at condensed-phase interfaces such as chemical reactions at solid/liquid interfaces1, 2) and electrochemical studies.3)

Recently, we found that an amphiphilic ruthenium (II) tris(bipyridine) homologue, RuCnB (n=16 or 18), could form a Z-type Langmuir-Blodgett (LB) monolayer assembly on an alkaline-treated glass substrate,4) probably due to electrostatic interaction between the hydrophilic head group and the glass surface. This indicates strong adsorptivity of the complex toward the glass surface. Since the metal complex of this type has a large molecular hyperpolarizability (70 x 10^{-30} esu for RuC18B5)) based on metal-to-ligand charge transfer transition, interfacial SHG will be observed if ordered alignment of the complex at any liquid/glass interfaces is attained. In the present paper, we report an in-situ observation of SHG from RuC12B at the interface of the ethylacetate solution and the alkaline-treated glass surface.

The experimental setup for the measurements of second harmonic (SH) signals is illustrated in Fig. 1. A standard quartz cell (10 x 10 x 40 mm) was fixed on a computer-controlled rotation stage (SIGMA KOKI MINI-60YAW, MINI-5P), whose vertical position could be adjusted by the use of a translation stage. The laser beam passed through the cell along the direction normal to the cell surface. A glass substrate (8 x 0.8 x 38 mm) was inserted into or removed from the quartz cell by moving both the substrate and the cell with respect to each other in vertical direction. The SHG measurement system was computer-controlled. The p-polarized second harmonic (SH) signal by the p-polarized excitation light was measured. In-situ measurements were carried out after a few minutes from substrate immersion; the SH signal had already reached constant. The glass substratre



RuCnB(n = 12, 16, 18)

was treated with fuming nitric acid, boiled in concentrated hydrochloric acid, soaked in a KOH-saturated ethanol solution, rinsed with deionized water, and dried at 70 °C, to obtain the alkaline-treated glass substrate.[4] The glass substrate treated with fuming nitric acid, on the other hand, was immersed in the octadecyltriethoxysilane (ODS)-anhydrous toluene (5 : 95 w/w) solution for one day at room temperature. Then the substrate was washed with chloroform, water, and dried at 65 °C for one day, to obtain the ODS-derivatized glass substrate. The ruthenium complex, RuC12B, was synthesized as described before.[6] Ethylacetate (Spectrozol, Dojindo) was used as received. Absorption spectra were recorded on a Shimadzu UV-2200 spectrophotometer. All measurements were carried out at 18 - 19 °C.

When the alkaline-treated glass substrate was rotated in a RuC12B (2.5×10^{-5} mol dm^{-3}) - ethylacetate solution, distinct interference fringe patterns of SH signals appeared as shown in Fig. 2a. The SH signal disappeared on removing the glass substrate from the solution. Since the front and the rear surface of the cell is fixed at normal to the laser beam, the effect of RuC12B adsorption at the cell surfaces on the observed SHG signal, if any, must be negligible.

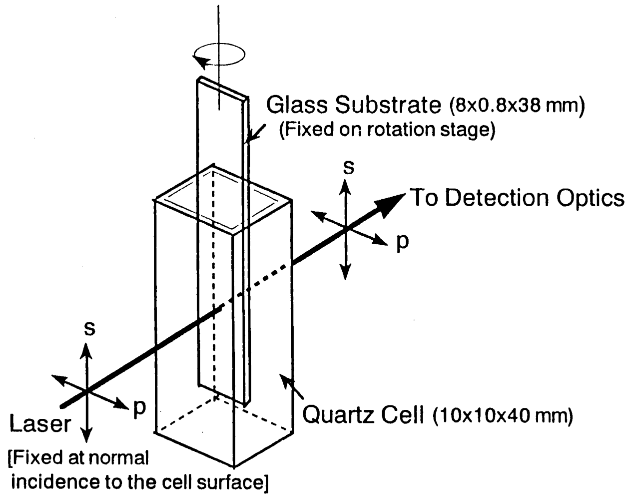


Fig. 1. Experimental geometry for SHG measurements.

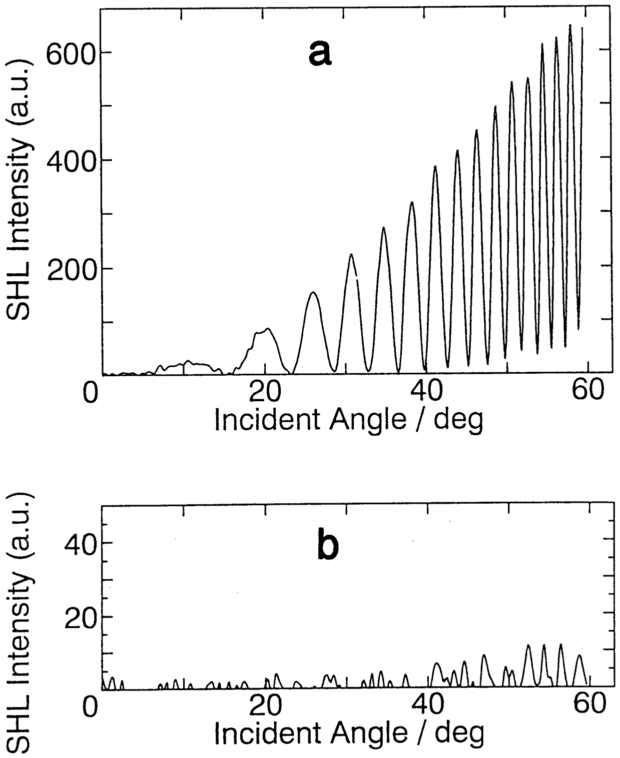


Fig. 2. Interference fringe patterns of SH signals by the rotation of the glass substrate in a RuC12B (2.5×10^{-5} mol dm^{-3}) - ethylacetate solution in a quartz cell: (a) alkaline-treated glass, and (b) ODS-derivatized glass.

The cell or the glass substrate itself also showed no appreciable SH signals. These results suggest that the SH signal originates from oriented RuC12B at the front and the rear interfaces of the glass substrate in contact with the bulk solution. On the other hand, rotation of the ODS-derivatized glass substrate in the same solution afforded no detectable SH signals (Fig. 2b). This indicates that RuC12B is not adsorbed to the interface between the solution and the hydrophobic ODS-derivatized surface.

After the measurements in the solution, the alkaline-treated glass substrate was withdrawn from the solution. The ruthenium complex thus should be deposited on the substrate. This substrate in air also gave the interference fringe patterns of the SH signals with comparable intensity but different fringe intervals as compared with those in the solution (Fig. 3a).7) The SH signal intensity was somewhat reduced by rinsing the withdrawn substrate twice with ethylacetate (Fig. 3b). Further rinsing did not affect the SH signal intensity. No appreciable SHG signals were observed with the ODS-derivatized glass substrate after withdrawal from the same solution.

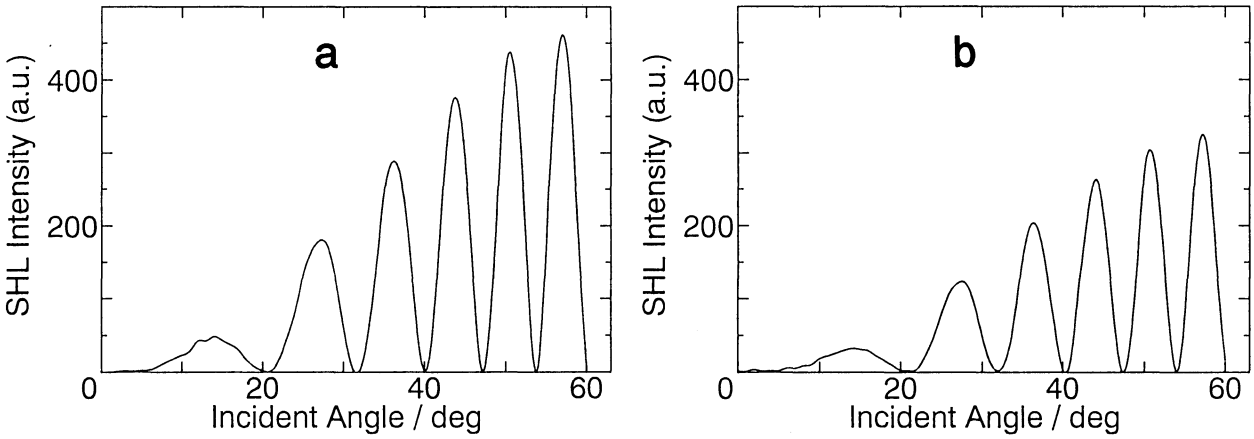


Fig. 3. Interference fringe patterns of the SH signals from the alkaline-treated glass substrate: (a) after withdrawal from the RuC12B (2.5×10^{-5} mol dm^{-3}) - ethylacetate solution, and (b) subsequent rinsing twice with ethylacetate.

Absorption spectral change of the glass substrate after withdrawal and the subsequent rinsing was concomitantly measured. As is recognized from Fig. 4a, RuC12B is deposited onto the alkaline-treated glass substrate. However, about

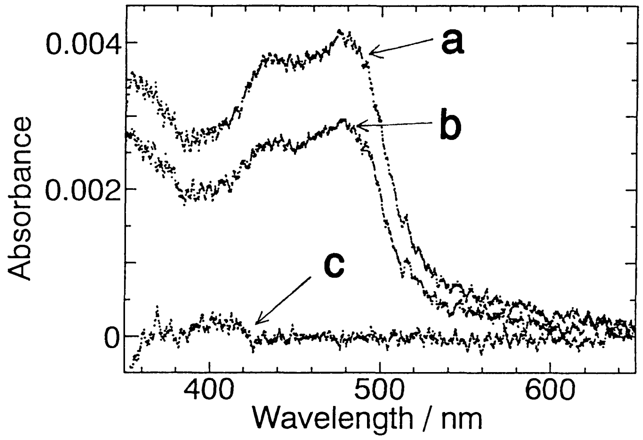


Fig. 4. Absorption spectra of the withdrawn glass substrates: the alkaline-treated glass substrate before (a) and after (b) rinsing with ethylacetate, and ODS- derivatized glass substrate before rinsing (c).

one-third of deposited RuC12B was rinsed off (Fig. 4b). This result is quite consistent with the reduction of the SH signal by rinsing twice (Fig. 3b). No deposition of RuC12B onto the ODS-derivatized substrate was also confirmed by the absoprtion spectra (Fig. 4c).

After rinsing twice with the solvent, the alkaline-treated substrate was immersed into the fresh solvent. As shown in Fig. 5, the SH signal profile roughly identical with that in the complex solution (Fig. 2a) reappeared, and the signal did not decrease with time.

These observations strongly suggest that RuC12B is adsorbed to the interfaces between the ethylacetate solution and the alkaline-treated glass surfaces. Some RuC12B must be additionally deposited onto the alkaline-treated glass surface in the withdrawing process by solvent evaporation of accompanied solution on the substrate. Adsorption of RuC12B on the alkaline-treated glass surface must be ascribed to electrostatic interaction between the dicationic head group of RuC12B and anionic surfaces (Si-O^-K^+) of the glass substrate. Quantitative and theoretical analysis of the SH signal properties are now in progress.

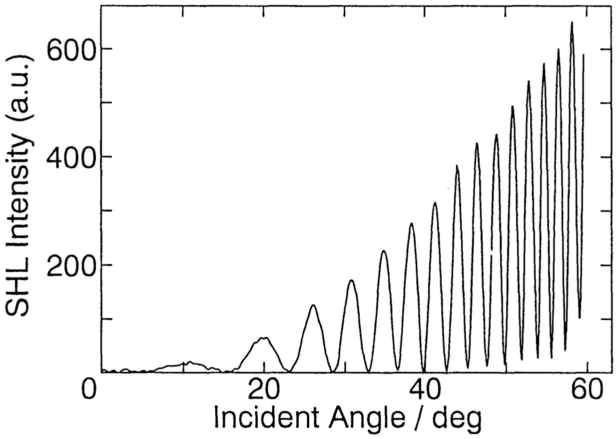


Fig. 5. Interference fringe patterns of the SH signals observed when the twice-rinsed alkaline-treated glass was immersed in fresh ethylacetate in the quartz cell.

The present study was partially supported by the Asahi Glass Foundation for Industrial Technology and Yazaki Memorial Foundation for Science and Technology, and by The Grant-in-Aid for Scientific Research (No. 04555199, 05650829, 05453192) from the Ministry of Education, Science and Culture.

References

1) S. Yitzchaik, S. B. Roscoe, A. K. Kakkar, D. S. Allan, T. J. Marks, Z. Xu, T. Zhang, W. Lin, and G. K. Wong, *J. Phys. Chem.*, **97**, 6958 (1993).
2) R. Yerushalmi-Rozen, J. Klein, and G. Berkovic, *Langmuir*, **8**, 1392 (1992).
3) R. M. Corn, *Anal. Chem.*, **63**, 285A (1991).
4) S. Yamada, T. Nakano, and T. Matsuo, *Thin Solid Films*, in press.
5) H. Sakaguchi, H. Nakamura, T. Nagamura, T. Ogawa, and T. Matsuo, *Chem. Lett.*, **1989**, 1715.
6) T. Matsuo, K. Takuma, Y. Tsutsui, and T. Nishijima, *J. Coord. Chem.*, **10**, 187 (1980).
7) Variation in peak separation of fringe patterns from Figs. 2 to 3 is ascribed to the difference in refractive index between the glass substrate (1.506) and the bulk medium (1.372 for ethylacetate in Fig. 2, and 1.000 for air in Fig. 3). Quantitative analysis by simulations of the fringe patterns is now in progress.

(Received February 24, 1994)