Letter

Effect of aliphatic tails on surface anchoring of amphiphilic ruthenium-polypyridine complexes in water-cast polymer films as studied by photoinduced electron-transfer and optical second harmonic generation

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Abstract

A thin poly(methyl methacrylate) (PMMA) film incorporating an amphiphilic ruthenium (Ru)-polypyridine complex having two (Ru2C16B) or four (Ru4C16B) aliphatic tails, and/or an amphiphilic viologen (LPV), was prepared on a water surface. Both interfacial and in-film photoinduced electron-transfer from the Ru-complex to LPV occurred more effectively in Ru2C16B as compared with Ru4C16B, suggesting more exposure of the hydrophilic head group of Ru2C16B at the film surface. Polarized optical second harmonic generation (SHG) studies on the Ru-complex-impregnated film also verified orientational difference between the two complexes; Ru4C16B tended to take more stand-up orientation as to the film surface. The SHG signal increased quadratically with the number of films in the presence of air gaps among them. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Photoinduced electron-transfer; Second harmonic generation; Thin polymer film

1. Introduction

Thin organic films are currently gaining much interest in many areas such as sensors and optoelectronic devices (see for example: [1]). Most of these tasks require the preparation of well-defined films composed of photofunctional molecules.

Previously, we developed a novel means of preparing thin polymer films incorporating an amphiphilic dye [2–7]. Studies on optical second harmonic generation (SHG) [2,4–7] as well as photocatalytic reactions [3] of the film incorporating the Ru-complex Ru2C16B showed preferential enrichment of the complex at the water-side surface (bottom side of the floating film on water) of the polymer film.

Previous investigations also verified that a poly(methyl methacrylate) (PMMA) film is thicker (50–70 nm) but more robust than a poly(vinylchloride) (PVC) film (20–30 nm), and the laminated film assembly gave good transparency [6]. Thus, PMMA can be practical than PVC in terms of practical film devices.

Ruthenium (II) (Ru)-tris (2,2′-bipyridine) (Ru(bpy)$_3$) homologues are excellent photosensitizers for artificial photosynthetic systems as well as for optoelectronic applications. Recently, we reported significant differences in monolayer structure of amphiphilic Ru(bpy)$_3$ homologues, Ru2C16B and Ru4C16B, having two and four aliphatic tails, respectively, at the air/water interface [8]. In this paper, a clear difference in the molecular alignment at the surface region of a PMMA film was also verified by photoinduced electron-transfer and polarized SHG experiments.

2. Experimental

Amphiphilic ruthenium(II)-polypyridine complexes with two (Ru2C16B) and four (Ru4C16B) n-hexadecyl groups, and viologen (LPV) were prepared in our laboratory [7,8]. Polymers, PMMA (Wako, MW 60000) and poly (ethylene glycol) (PEG: Tokyo Kasei n ~ 25) were used as received. Organic solvents were purified by distillation.

Self-standing thin polymer films incorporating the dyes

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were prepared on water as before [7]. For example, the solution for preparing the PMMA film consists of PMMA (0.11 g), PEG (0.5–1 wt.% to PMMA), and a chloroform: toluene (1:1 v/v) solvent. The thin PMMA film formed quickly on spreading ~10 μl of this solution over the water surface. The floating film was picked up by the use of an appropriate frame. Accordingly, self-standing thin film was obtained in the frame. The film thickens is ~50–70 nm [7].
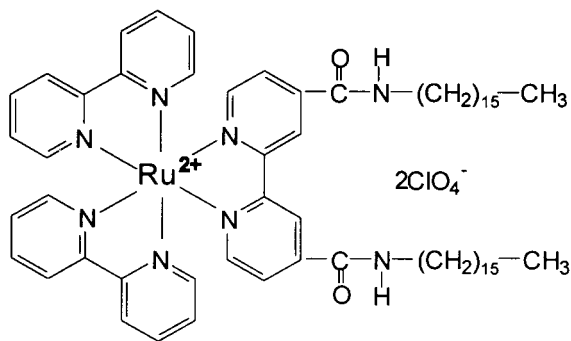
Ru2C16B
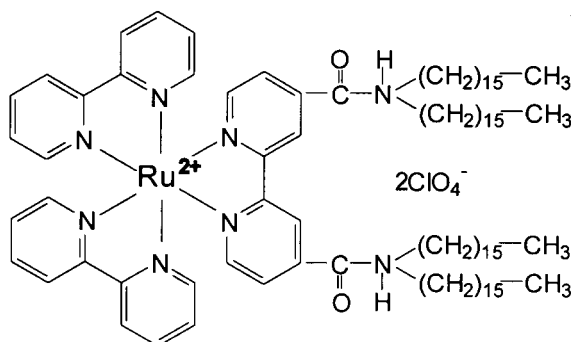
Ru4C16B
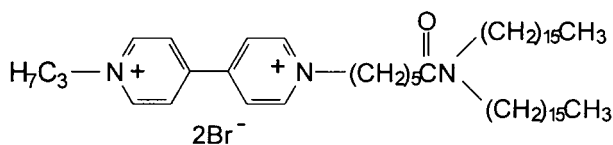
LPV

Absorption and luminescence spectra were measured with a Shimadzu UV-2200 spectrophotometer and a Hitachi F-3010 fluorescence spectrophotometer, respectively. Excitation and emission wavelengths are 470 and 620 nm, respectively.

The experimental setup for SHG measurements is iden-

tical to the one described previously [4]. Briefly, p- or s-polarized fundamental light (1064 nm) from a Nd:YAG laser (~20 mJ, 7 ns, 10 Hz) was employed to irradiate the sample, and the p- or s- polarized component of the transmitted second harmonic (SH) component was detected by the time-gated detection equipment. The s-polarized component was negligibly small.

3. Results and discussion

Absorption spectra of the Ru-complex-impregnated PMMA films are shown in Fig. 1; in each complex, two sheets of independently prepared films are measured to test the reproducibility. The average concentration of the Ru-complex in the PMMA film is calculated to the $~2.2 \times 10^{-2}$ M, provided that all complexes in the 10 μl solution (1×10^{-3} M) for film preparation is incorporated into the film. From absorption spectra and molar absorptivity (ε) of the Ru-complex ($\varepsilon \sim 1.4 \times 10^4$ M^{-1} cm^{-1} at the absorption maximum (~450 nm) of the change-transfer band in methanol), the concentration of the Ru-complex in the PMMA film of $\sim$ 50–70 nm thickness is estimated to be ($\sim$ 3–2) $\times 10^{-2}$ M, consistent well with the above calculation.

The Ru-complex - viologen couple is a typical redox pair for a photoinduced electron-transfer ET reaction [9]. Asymmetric population of the dye was verified from photoinduced ET investigations. Two types of double-layered film assemblies (A and B in Fig. 2) were prepared by laminating the Ru-complex- and the LPV-impregnated films in different orientations as to the film surface: face-to-face (A) and sitting-on-top (B) type lamination as to the water-side surface [7]. In the film C, both the Ru-complex and LPV are incorporated in the PMMA film. In all film assemblies, the concentration of the Ru-complex is identical (5×10^{-4} M in the mixed solution: see experimental section), while that of LPV is changed from 0–2×10^{-3} M. In the case of Ru2C16B, the hydrophilic head group is larger in size (~0.9 nm^2 cross-section from CPK molecular model) than the sum of pendant two n-hexadecyl groups (~0.2 nm^2 for one n-hexadecyl group). Judging from the area of the cubic head group of Ru2C16B and from the film thickness (~50–70 nm), the coverage of water-side surface by the head group is estimated to be ~30–40%, if one assume that all Ru2C16B are aligned at the water-side surface with their head groups pointing to the surface as schematically shown in A–C of Fig. 2. A similar estimation is possible in the film C incorporating both Ru2C16B and LPV (~0.4 nm^2 cross-section for the viologen moiety); the hydrophilic moieties of Ru2C16B and LPV are expected to saturate (coverage: ~110–80%) at 5×10^{-4} M of Ru2C16B and 2×10^{-3} M of LPV (as the concentrations of the solution for film preparation).

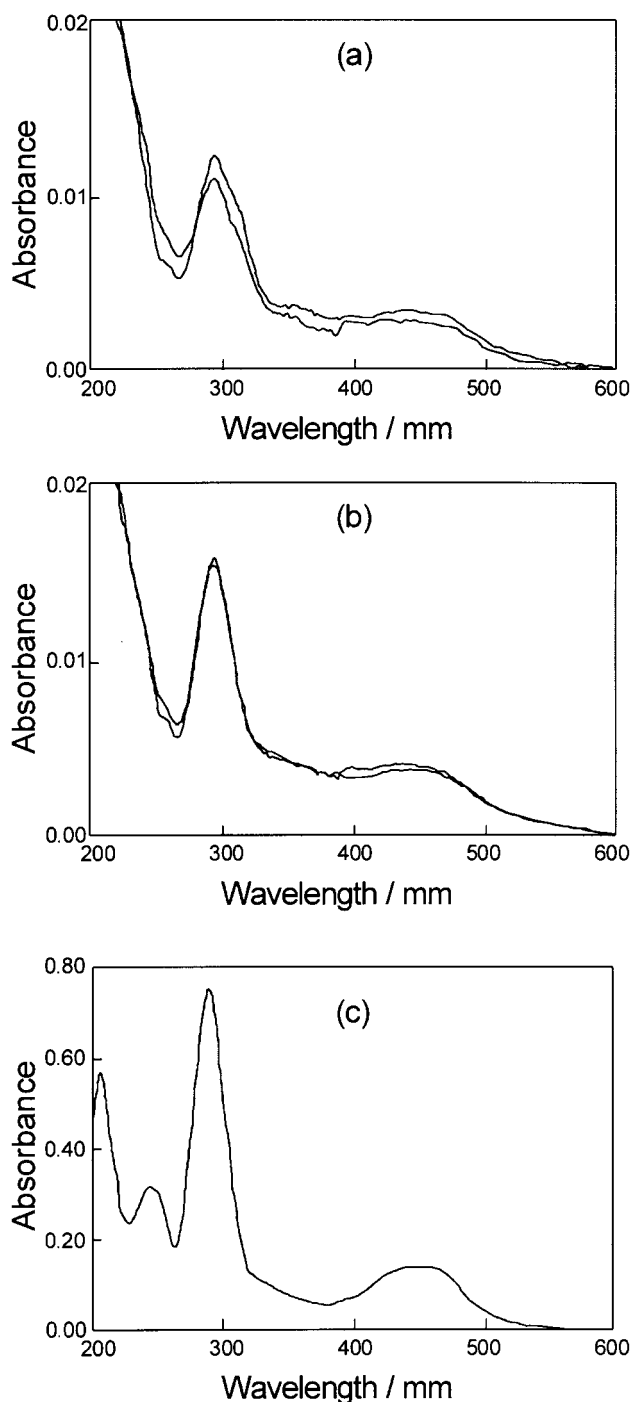The luminescence quenching of the Ru-complex by LPV

Fig. 1. Absorption spectra of (a) Ru2C16B- and (b) Ru4C16B-impregnated PMMA films; in each complex two sheets of independently prepared films are compared. The absorption spectrum of Ru4C16B in methanol (1×10^{-5} M) is also shown (c).

was compared at the three film samples shown in Fig. 2. The luminescence of the Ru-complex was hardly quenched in the case of B-type lamination, indicating that the Ru-complex and LPV are separated enough to avoid photoinduced ET. In the case of A-type lamination, on the other hand, the luminescence of Ru2C16B (Fig. 2a, (●)) was

substantially reduced with increasing the LPV concentration. This suggests that the hydrophilic head group of Ru2C16B and the 4,4′-bipyridiuim moiety of LPV are preferentially populated at the water-side surface of the films, so as to be able to close each other enough for photo-induced ET across the film-film interface. On the contrary, the luminescence of Ru4C16B was less quenched even in the case of A-type lamination as shown in Fig. 2b (●). Thus, the head group of Ru4C16B may not be so exposed to the surface as to occur photoinduced ET to the bipyridinium moiety of LPV incorporated in the neighbor film.

The luminescence of Ru2C16B was effectively quenched when Ru2C16B and LPV were incorporated in the same film (C-type film) as shown in Fig. 2a (■); the quenching reached constant at as low as 5×10^{-4} M of LPV. These aspects suggest that both hydrophilic moieties of Ru2C16B and LPV are preferentially populated at the water-side surface, and that the photoinduced ET in the surface occurs effectively rather than across the film-film interface. In the case of Ru4C16B the luminescence is less quenched by LPV even in the C-type film, implying that the head group of Ru4C16B is not so close to the bipyridinium moiety of LPV in the film, as compared with the case of Ru2C16B. In Ru4C16B, the cross-sectional sum of the four n-hexadecyl groups is quite comparable with the cross-section of the head group. Probably, the hydrophobic as well as the steric effects of the pendant four n-hexadecyl groups will hinder the close packing of the hydrophilic head groups at the film surface, while the bipyridinium moiety of LPV will be exposed at the surface.

The SHG technique is very useful for studying molecular orientation of an asymmetrically populated molecular assembly. Since the Ru-complex of this type is SHG-active [2], the SHG technique can be applicable for investigating orientation of the complex when they are non-centrosymmetrically distributed at the film surface.

As shown in Fig. 3, polarized SH signals were clearly observed from the Ru-complex-impregnated film. No s-polarized SH components were observed. In the projection model, the transmitted SH component I_{pp} (p-polarized SH component induced by p-polarized fundamental light) is given by

$$I_{pp} \propto \left(3/2\tan^2\Theta\sin\theta\cos\theta + \sin^3\theta\right)^2 I_0^2 \qquad (1)$$

where θ and Θ show the incident angle of the laser light with the intensity of I_0 and the average tilt angle of molecular hyperpolarizability, respectively [10,11]. The solid line is the best fit to the Eq. (1), talking $\Theta = 49°$ for Ru2C16B and 35° for Ru4C16B. The Θ value can also be evaluated from the ratio of SH components as [10,11]

$$\frac{I_{pp}}{I_{ps}} = \frac{1}{4}\left(3 + \frac{\sqrt{2}}{\tan\Theta}\right)^2$$

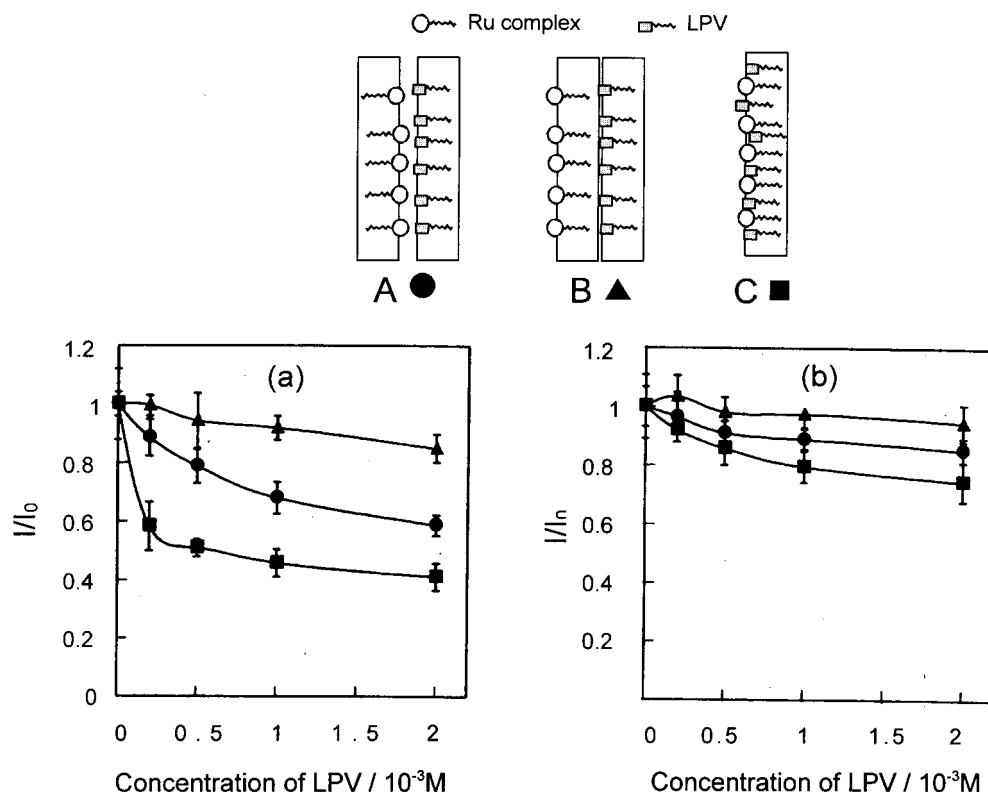From Fig. 3a, the Θ value was evaluated to be ~47°,

Fig. 2. Luminescence quenching of the Ru-complex by LPV: (a) Ru2C16B; (b) Ru4C16B. Two types of double-layered film assemblies (A, B) incorporating the Ru-complex and LPV, respectively, are shown: water-side surfaces are aligned in face-to-face (A) and in the same direction (B). In the single film (C), both the Ru-complex and LPV are incorporated.

close to 49°. As to Ru4C16B, I_{sp} was negligibly small as shown in Fig. 3b. Thus, the Θ value is expected to be smaller than 35°. The results indicate that Ru4C16B anchors at the surface region of the film, where its molecular axis is stand-up more steeply as to the film surface, in comparison with Ru2C16B. Similar results for the both complexes have also been obtained at the air/water interface [8] at a higher surface pressure. In the case of the Langmuir method, the monolayer is prepared at the compressed condition. In the present case, however, the film is formed only by spreading the solution on the water surface. Nevertheless, Ru4C16B can take rather stand-up orientation as compared with Ru2C16B, probably due to effective anchoring by the four *n*-hexadecyl groups.

The SH signal from the Ru-complex-impregnated film was also measured when the blank film (without dye molecules) was laminated on the water-side (Fig. 4a) or its opposite-side (Fig. 4b) of the Ru-complex-impregnated film. Lamination of the blank film at the water-side surface of the Ru-complex-impregnated film reduced the SH response, the ratio of SH signal (I_{pp}) in the absence (I_{pp}^a) to the presence (I_{pp}^b) of the blank film, I_{pp}^a/I_{pp}^b, was larger for Ru2C16B (5.5) than for Ru4C16B (3.5). This also indicates that the orientation of SHG-active Ru(bpy)$_3$-moiety of Ru2C16B is substantially deteriorated by the lamination of the blank film, as compared with the case of Ru4C16B. The result is quite consistent with the photoinduced ET experiment (Fig.

2), and thus the Ru(bpy)$_3$ moiety of Ru2C16B is more exposed to the film surface.

Previously, we reported similar SHG results using poly(-vinylchloride) (PVC) film [4]. The PMMA film is thicker but more robust than the PVC film, and the laminated film assembly was satisfactory transparent. Thus the PMMA can be practical in terms of optoelectronic devices. However, the present results show that even in PMMA direct lamination of the films induces appreciable modification of the surface alignment of the Ru-complex relevant to SHG. Thus, stacked film assemblies with air gaps (0.2 mm) were prepared and their SH responses were measured as a function of the number of films. As shown in Fig. 5, the SH signal increased quadratically with the number of films. The thickness of the film (50–70 nm) as well as the total length of air gaps ($\sim$0.8 mm) are much less than the corresponding coherence lengths of PMMA ($\sim$ the order of micrometers) [12] and air ($\sim$13 cm [13]). Thus the non-linear polarization of the films can be simply summed up when the films are stacked with spatial separation.
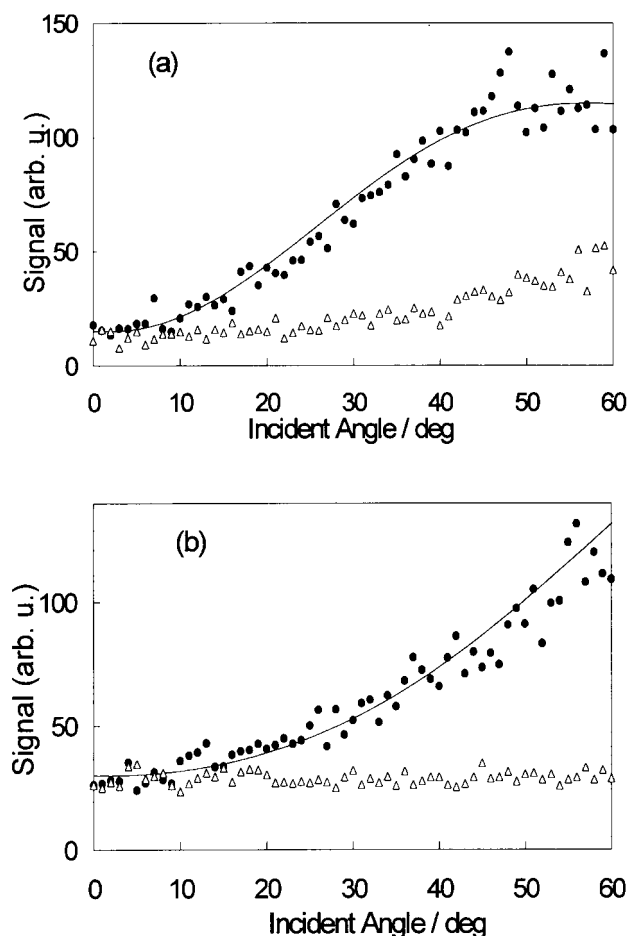
Fig. 3. Angular dependencies of the SH signals from (a) Ru2C16B- and (b) Ru4C16B-impregnated films: (●), I_{pp}; (△), I_{sp}. The solid line slows the heat fit to Eq. (1) for $\Theta = 47°$ (a) or $35°$ (b).
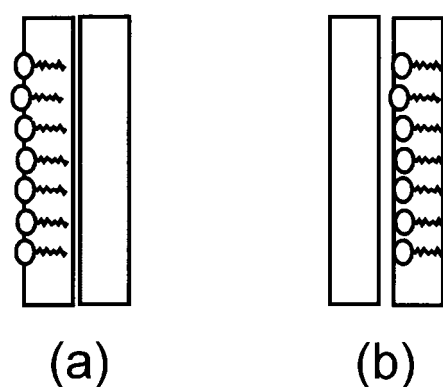

Fig. 4. Double layered assemblies of the Ru-complex-impregnated film and the blank film; the blank film is laminated on the water-side (a) or the opposite side (b) of the Ru-complex-impregnated film.
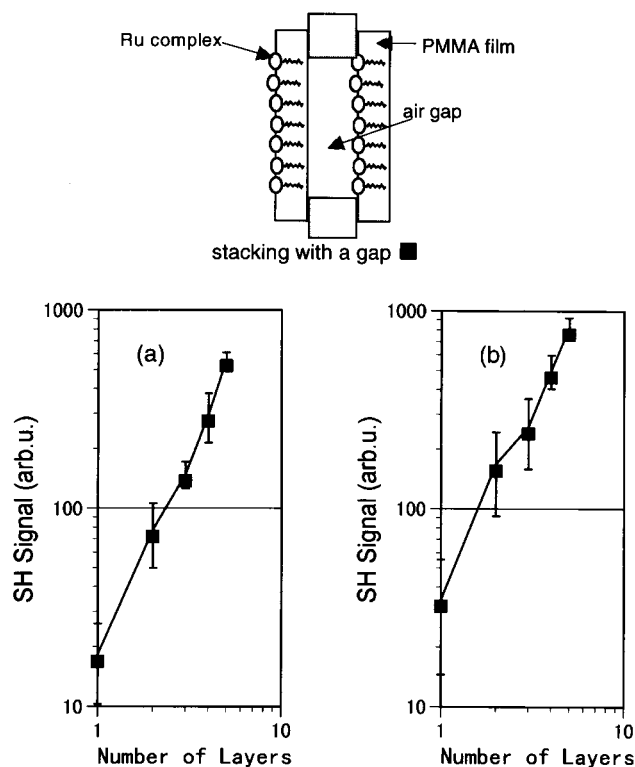

Fig. 5. Relationships between SH signals and the number of films in sitting-on-top type alignments with a 0.2-nm air gap between each film (as schematically shown at the top in the case of two sheets at the top.): (a), Ru2C16B; (b), Ru4C16B.

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