

Asymmetric Property of an Ultrathin Polymer Film impregnated with Amphiphilic Polypyridine Complex for Photocatalytic Reduction of Viologen

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Only one surface of an ultrathin polymer film impregnated with an amphiphilic ruthenium(II) tris(bipyridine) complex functioned in the photocatalytic reduction of viologen, showing that the film surface had an asymmetric property which was determined by the population of metal complex.

The development of ultrathin films which function as photoredox sites is one of the most important key steps in the study of photochemical energy conversion relevant to studies on photosynthesis. A number of chromophore-containing Langmuir-Blodgett (LB) membranes have been prepared and their photochemical characteristics have been studied with this in mind.¹ A novel method for preparing an ultrathin polymer film has been developed by Kajiyama and his associates.² For example, an ultrathin poly(vinyl chloride) (PVC) film (*ca.* 25 nm thickness) can be obtained by spreading an organic solution of PVC over a water surface. In a similar manner, we have prepared a PVC film impregnated with an amphiphilic ruthenium(II) polypyridine complex.³ The film preparation is

easy and a self-supporting film can be obtained with the aid of an appropriate frame. A highly asymmetric orientation of the ruthenium complexes in the film was suggested by second harmonic generation studies.³ We have now investigated the photochemical behaviour of this ruthenium-complex-impregnated ultrathin film.

PVC (degree of polymerization, 1100) was purified by precipitation from tetrahydrofuran (THF)-methanol. The amphiphilic ruthenium(II)-tris(bipyridine) complex, **RuC16B**,⁴ and the zwitterionic viologen, **4ZV**,⁵ were synthesized. The solution for making ultrathin PVC films was prepared by dissolving 0.1 g of PVC in 2 ml of a toluene-THF (1:1 v/v) solution containing 1.5 mmol l⁻¹ of **RuC16B**. The ultrathin

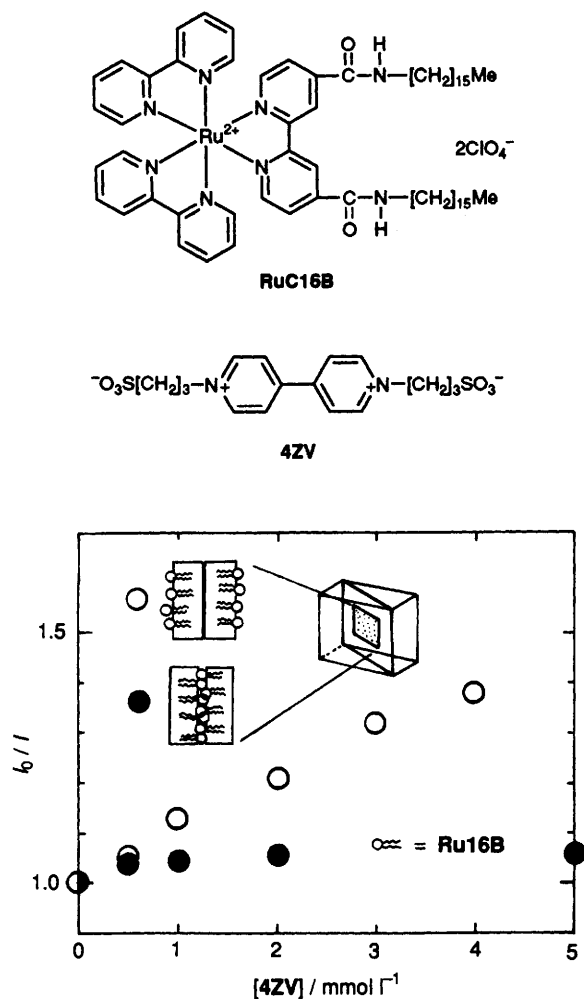


Fig. 1 Luminescence quenching by 4ZV of RuC16B incorporated in PVC films: Concentration of [RuC16B] 1.5 mmol l^{-1} . Lamination conditions of the films: \circ top sides and \bullet bottom sides of the two films face each other.

film formed quickly on spreading $10 \mu\text{l}$ of the solution over a pure water surface. The floating film was picked up by the use of a polyester frame.

The contact angle of a water droplet on the bottom side (*i.e.* the side of the polymer-water interface in the film preparation process) was 66° , while that on the opposite (top) side (*i.e.* the side of the air-polymer interface) was 77° . The latter value was similar to values obtained for both sides of the film without RuC16B. These results indicate that the hydrophilic head group of RuC16B is preferentially located at the polymer-water interface (bottom side of the film).

Luminescence quenching of RuC16B incorporated in the PVC film by 4ZV was investigated using two types of double-layer film assemblies in different film orientations; the top sides or the bottom sides of two films faced each other in accordance with the laminating direction of the self-supporting PVC films in polyester frames ($20 \times 20 \text{ mm}$). The laminated film assembly was fixed in a quartz cell ($10 \times 40 \text{ mm}$) as shown in Fig. 1. The luminescence intensity of RuC16B clearly decreased with increasing 4ZV concentration, when the bottom sides of the films were exposed to the 4ZV solution. The quenching obeyed a simple Stern-Volmer relationship with a Stern-Volmer constant of 100 l mol^{-1} . The luminescence lifetime of RuC16B in the film was $1.0 \pm 0.1 \mu\text{s}$, so that the quenching rate constant was calculated to be $10^8 \text{ l mol}^{-1} \text{ s}^{-1}$. This value is one order of magnitude smaller

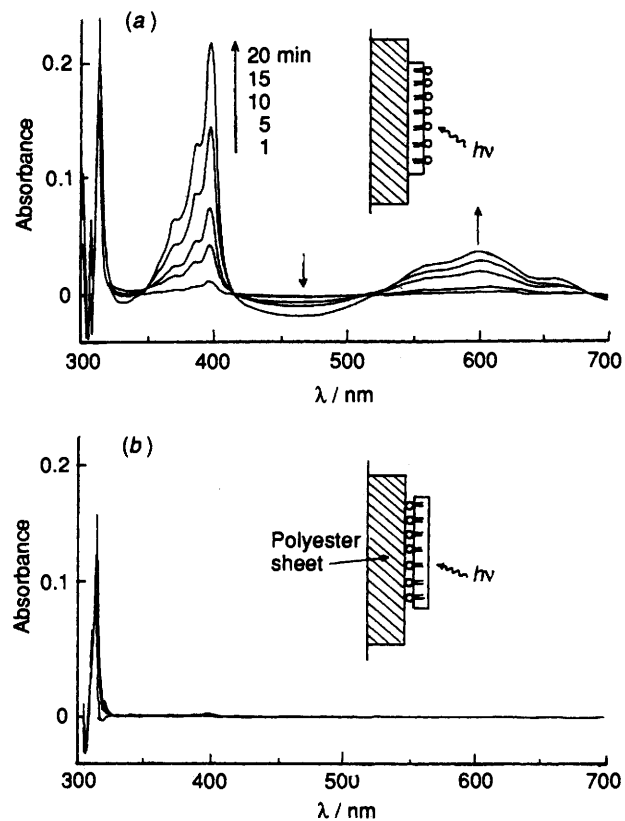
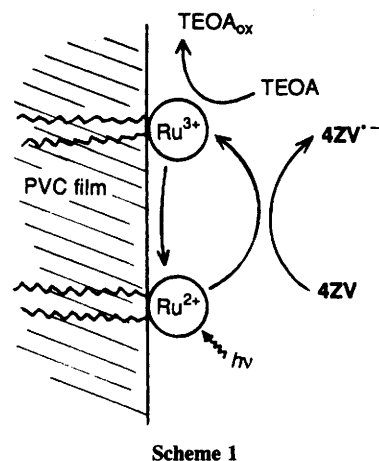


Fig. 2 Photoinduced reduction of 4ZV by RuC16B incorporated in the PVC film in the presence of TEOA as sacrificial reductant: $c/\text{mmol l}^{-1}$: RuC16B, 1.5; 4ZV, 1; TEOA, 10. Film orientation: (a) bottom side is exposed to the solution, and (b) bottom side is shielded from the solution.



Scheme 1

than that for the ruthenium(II) tris(bipyridine) 2^+ -4ZV system in an aqueous solution.⁴

In the case of the film assembly with top-side exposure, no appreciable quenching was observed. These findings show that the hydrophilic head group of RuC16B is preferentially located at the bottom side of the film and most likely exposed to the polymer-water interface.

Photocatalytic reactions were carried out using a single-layer film in a standard quartz cell ($10 \times 10 \text{ mm}$). We prepared two types of a single-layer film in different orientations: the top side or the bottom side of the film was protected from the reaction solution by putting the film on a transparent polyester sheet ($9 \times 40 \times 0.1 \text{ mm}$). This film assembly was immersed in the reaction solution in the cell. After the reaction solution

had been deaerated with argon gas for 20 min, it was illuminated with a 300 W high-pressure Hg arc lamp through a visible-pass glass filter (>430 nm). The film did not peel off the polyester sheet during the measurements. Fig. 2(a) shows absorption spectral changes during illumination of the reaction cell containing the film assembly, **4ZV** (1 mmol l^{-1}), and triethanolamine (TEOA) (10 mmol l^{-1}) as the sacrificial reductant. When the bottom side of the film was exposed to the reaction solution, characteristic absorption bands due to the viologen anion radical appeared at 370, 385, 397, 560, 600 and 660 nm which grew with illumination time. At the same time, the absorption band due to **RuC16B** (centred at 470 nm) decreased slightly. Reduction of **4ZV** did not occur in the absence of TEOA. The spectrum reverted completely to its initial state by subsequent aeration. These results clearly indicate that photocatalytic reduction of **4ZV** by **RuC16B** proceeds with on illumination, as shown in Scheme 1. As in the case of luminescence quenching, no appreciable change in the absorption spectrum was observed when the bottom side of the film was protected by the polyester sheet [Fig. 2(b)].

Thus, the photoredox reaction also confirmed that the population of amphiphilic **RuC16B** is highly asymmetric with respect to the film surface and the hydrophilic head group is preferentially concentrated on its bottom side.

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References

- 1 See for example: D. Mobius and H. Mohwald, *Adv. Mater.*, 1991, **3**, 19.
- 2 H. Kikuchi, A. Kumano, T. Kajiyama, M. Takayanagi and S. Shinkai, *Rept. Prog. Polym. Phys. Jpn.*, 1984, **27**, 273.
- 3 T. Matsuo, H. Nakamura, T. Nakao and M. Kawazu, *Chem. Lett.*, 1992, 2363.
- 4 T. Matsuo, K. Takuma, Y. Tsutsui and T. Nishijima, *J. Coord. Chem.*, 1980, **10**, 187.
- 5 T. Nagamura, T. Kurihara, T. Matsuo, M. Sumitani and K. Yoshihara, *J. Phys. Chem.*, 1982, **86**, 4368.
- 6 T. Ohsako, T. Sakamoto and T. Matsuo, *J. Phys. Chem.*, 1985, **89**, 222.