A Porphyrin-Anchored Ultrathin Poly(vinylchloride) Film: Asymmetric Surface Property as Revealed by Interactions with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

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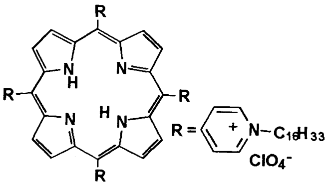
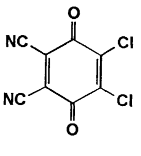
An ultrathin poly(vinylchloride) film incorporating amphiphilic 5,10,15,20-tetrakis(4-N-hexadecylpyridyl)porphine at the surface was prepared. Asymmetric surface population of the porphyrin was confirmed by investigating interactions with 2,3-dichloro-4,5-dicyanobenzoquinone in aqueous solutions, using absorption, fluorescence, and in-situ second harmonic generation spectroscopy.

Fabrication of monolayer assemblies at surfaces with desired physicochemical properties such as second harmonic generation (SHG) and photocatalytic activity are very important subjects in scientific and technological fields. Porphyrin is one of the best compounds for implanting such properties to monolayer assemblies. The Langmuir-Blodgett (LB) method has been successful for fabricating porphyrin monolayer assemblies on solid surfaces.[1] Fixation of pophyrin monolayer assemblies, which exhibit distinct nonlinear optical (NLO) property, on the SiO_2 surface via covalent bonding has been reported.[2] However, fabrication of these films have been restricted to some specified substrates.

Poly(vinylchloride) (PVC) was found to form an ultrathin film on a water surface.[3] In a similar manner, we recently developed a method of preparing ultrathin PVC films (ca. 25 nm thickness) with substantial NLO response[4] as well as photocatalytic activity.[5] The films were obtained by spreading a small amount of an organic solution containing PVC and an amphiphilic ruthenium (II)-polypyridine complex on a water surface; the complex was oriented in the ultrathin film matrix. In the present study, we have succeeded in incorporating an amphiphilic 5,10,15,20-tetrakis(4-N-hexadecylpyridyl)porphine, H2C16TPyP in the PVC film. Preferential population of the porphyrin at one film surface was confirmed from the interactions with 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ) in aqueous solutions.



H2C16TPyP



DDQ

The amphiphilic porphyrin (H2C16TPyP) was prepared in a similar manner as described before.[6] Other chemicals were used as received. The solution for making a H2C16TPyP-impregnated PVC film was prepared by dissolving 0.1 g of PVC in 2 ml of a THF - toluene (1:1 v/v) solution containing 1×10^{-3} mol dm^{-3} (= M) of H2C16TPyP. The film was quickly formed by carefully spreading 10 μl of the solution on a pure water surface, and the floating film was picked up by using an appropriate frame.[7]

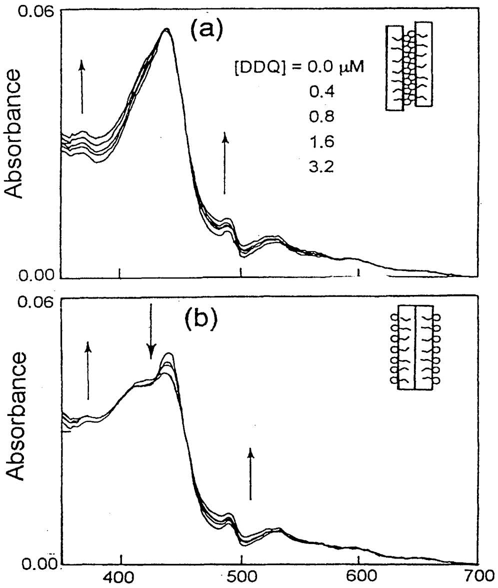


Figure 1. Absorption spectra of double-layered PVC film assemblies containing H2C16TPyP in aqueous DDQ solutions: (a) bottom-sides or (b) top-sides of the films face each other as shown in the insert. DDQ concentrations are denoted in the figure.

Absorption spectral changes of the PVC film containing H2C16TPyP by the addition of DDQ were investigated with double-layered film assemblies in two-different film-orientations as shown in the insert of Figure 1. The film surfaces were defined in accordance with the method of preparation: the upper surface of the floating film on water was named as the top-side, and the lower one as the bottom-side. The double-layered film assembly self-supported in a polyester frame (area: 5 × 18 mm) was immersed into an aqueous DDQ solution in a standard quartz cell (10 × 10 × 40 mm). The spectra in Figure 1a were obtained with double-layered film assembly in face-to-face stacking of the bottom-sides, while the top-sides of two films faced each other in Figure 1b. In the case of the film assembly with top-side exposure (a), the Soret band of the porphyrin changed only slightly with increasing DDQ concentration. In the case of the film assembly with bottom-side exposure (b), on the other hand, the Soret band changed even on immersion into water[8], and further decreased clearly as the DDQ concentration increased. This result clearly indicates that the porphyrin moiety is preferentially enriched to the bottom surface of the film, where noticeable π-electronic interaction between the porphyrin moiety and DDQ was possible.

Fluorescence quenching of H2C16TPyP incorporated in the film was also investigated by the use of double-layered film as-

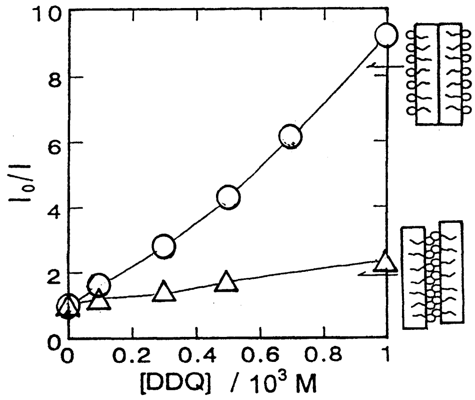


Figure 2. Fluorescence quenching of H2C16TPyP incorporated in the PVC film, on exposure to the DDQ solution. Lamination condition of the films are identical to those in Figure 1.

semblies with 20×20 mm area in a polyester frame (vide supra). The film assembly was fixed in a quartz cell (10×40×40 mm)[5], and the DDQ concentration was varied. The fluorescence intensity clearly decreased with increasing DDQ concentration in the film assembly with bottom-side exposure, but not significantly in the case of top-side exposure, as shown in Figure 2. This is quite consistent with the results of absorption measurements.

The experimental setup for the measurements of in-situ second harmonic (SH) signals is almost identical to the one described previously.[9] A PVC film was supported in a polyester frame (area: 15×30 mm), which was fixed to a computer-controlled rotation stage, and the whole film assembly was immersed into the DDQ solution in a glass cell (20×20×40 mm). The laser beam passed through the cell along the direction normal to the cell surface. The transmitted p-polarized SH signal, as induced by the p-polarized excitation light, was measured.

The SH signal was clearly observed when the H2C16TPyP-impregnated PVC film was rotated in the aqueous DDQ solution as typically shown in the case of 9×10^{-6} M (Figure 3a). In the absence of DDQ, no appreciable SH signals were observed from the H2C16TPyP-impregnated film. The blank film (without H2C16TPyP) also showed no appreciable SH signal, even in the presence of DDQ. The background signal (ca. 20 (arbitrary units)) in each case, which may be due to stray and scattered lights, and to some electrical noises, should be subtracted from the observed signal in discussing the actual SH signal intensity.

As shown in Figure 3b, the SH signal at an incident angle of 57° increased with DDQ concentration. Curiously, the SH signal tended to decrease at higher DDQ concentrations. The reason is not apparent at this stage; reabsorption of the SH signal by DDQ may be small judging from molar absorptivity at 532 nm (~500 M^{-1}cm^{-1}). No appreciable SH signals were observed in the case of anthraquinone-2,6-disulfonic acid in water. These results strongly indicate that the NLO response is attributed to intermolecular donor-acceptor charge transfer between π-electronic systems of the porphyrin moiety and DDQ, and the effect of asymmetric orientation of DDQ at the film surface on the NLO response is negligible.

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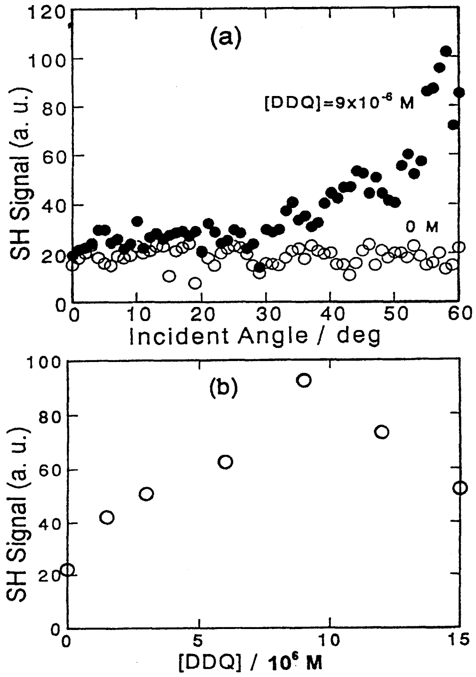

Figure 3. (a) Angular dependence of the in-situ SH signals from the H2C16TPyP-impregnated PVC film in the presence (●) and absence (○) of DDQ (9×10^{-6} M). (b) In-situ SH signals at 57° (incident angle) as a function of DDQ concentrations in water.

References and Notes

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7 The average concentration of H2C16TPyP in the PVC film was estimated to be 1.5 × 10^{-2} M, provided that all H2C16TPyP was incorporated into the film. Contact angles of water droplets on the top- and bottom sides of the film were 80° and 73°, respectively, which indicated preferential location of the porphyrin ring at the bottom side.

8 It is not apparent at this stage why the absorption spectrum of H2C16TPyP-impregnated film changes in air and in water.

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