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Structural Change of Pheophorbide *a* Methyl Ester by Contact with Titanium Oxide Particles

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Pheophorbide *a* methyl ester, which was derived from natural chlorophyll *a*, was converted to purpurin-18 methyl ester by contact with titanium oxide particles in the presence of oxygen under mild conditions in the dark.

Utilization of solar energy is a promising strategy to overcome energy and environmental crises. From this viewpoint, dye-sensitized solar cells (DSSCs) have attracted much attention recently,[1–3] since they can be produced with low-cost and low-energy processes. To date, various photosensitizers for DSSCs have been developed.[4–6] Among them, ruthenium complexes were reported to function as good photosensitizers of DSSCs.[6–9] Organic dyes have also been employed as DSSC photosensitizers that are free from rare metals.[6,10–13] However, many organic dyes can hardly absorb near-infrared light, resulting in the limitation of application to DSSCs.

Chlorophylls (Chls), which are abundant photosynthetic pigments in nature, and their derivatives have been regarded as potential photosensitizers in DSSCs,[4–6,14–19] since these molecules can capture photons in visible and near-infrared regions. In addition to the advantage of such spectral properties, Chls can be easily prepared from higher plants and algae. The molecular structure of Chl *a* is shown in Figure 1A. Chl *a* possesses central magnesium and a phytyl chain at the 17-propionate. Since naturally occurring Chl *a* is unstable, stable Chl derivatives, which are modified from Chl *a*, have been widely examined as photosensitizers of DSSCs.[14–19] However, little attention has been paid to molecular states of Chl derivatives on TiO_2 electrodes and their potential denaturation. In the present study, we report a unique structural change of a Chl derivative by contact with TiO_2 particles in the presence of molecular oxygen in the dark.

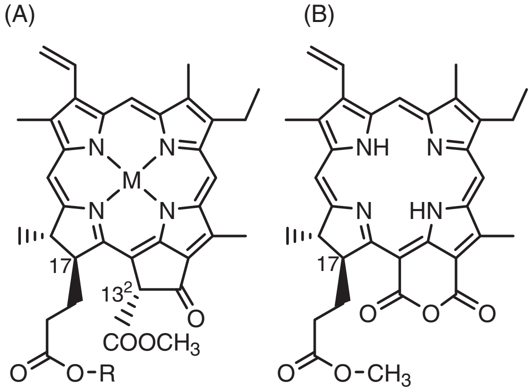

Figure 1. (A) Molecular structures of Chl *a* (M = Mg, R = phytyl) and pheophorbide *a* methyl ester (**1**, M = 2H, R = CH_3). (B) Molecular structure of purpurin-18 methyl ester (**2**).

Pheophorbide *a* methyl ester (**1**) was used as a model compound of Chl derivatives in this study, because of their stability and easy preparation. The molecular structure of **1** is shown in Figure 1A. Structural differences between **1** and natural Chl *a* are central atoms in the chlorin macrocycle and esterifying chains: **1** lacks central magnesium (M = 2H in Figure 1A) and has methyl ester (R = CH_3 in Figure 1A) instead of phytyl ester in Chl *a*. Pheophorbide *a* methyl ester (**1**) was synthesized from Chl *a*, which was extracted from a cyanobacterium *Spirulina geitleri*, through two steps according to previous reports.[20,21] Anatase-type TiO_2 particles, which were purchased from Wako Pure Chemical Industries, Ltd. (diameter; 5 µm, purity; 99.9%), were added to a CH_2Cl_2 solution of **1**, and stirred for 4 h at room temperature in the dark. Figure 2 depicts spectral changes of supernatants of the CH_2Cl_2 suspension of **1** containing TiO_2 particles. Soret and Q_y absorption bands of **1**

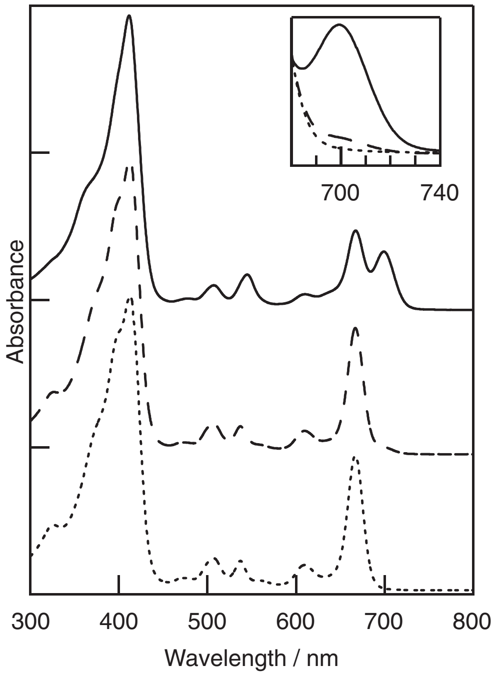

Figure 2. Visible absorption spectra of supernatants of CH_2Cl_2 suspensions of pheophorbide *a* methyl ester (**1**) by bubbling air for 4 h (solid curve), by bubbling N_2 for 4 h (broken curve), and intact **1** in CH_2Cl_2 (dotted curve). These spectra were normalized at Soret absorption bands. Insert: overlay of three spectra between 680 and 740 nm.

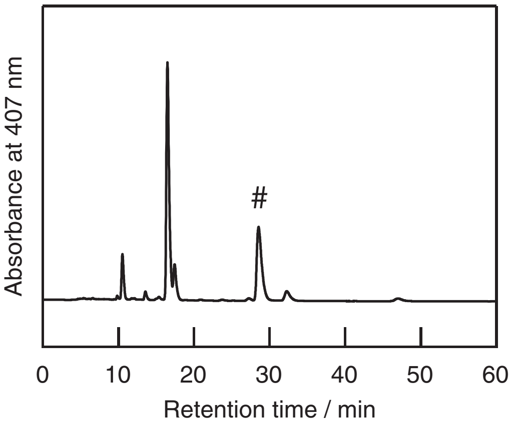

Figure 3. HPLC chromatogram of reaction products in the supernatant of a CH_2Cl_2 suspension of pheophorbide *a* methyl ester (**1**) by bubbling air for 4 h. The products were eluted on $5C_{18}$-AR-II (6 mmϕ × 250 mm) with methanol at a flow rate of 1.0 mL min^{-1}. The fraction denoted by # was the 700-nm absorbing compound.

were positioned at 413 and 667 nm, respectively, before stirring with TiO_2 particles. When the suspension of **1** and TiO_2 particles was bubbled with air for 4 h, a new Q_y absorption band appeared at 700 nm. In contrast, the absorption band around 700 nm was hardly observed by bubbling nitrogen gas for 4 h. No spectral change of **1** was detected by bubbling air without TiO_2 particles (data not shown). These indicate that the 700-nm absorbing product was generated from **1** in the presence of TiO_2 particles and molecular oxygen.

The supernatant of the CH_2Cl_2 suspension of **1** and TiO_2 particles by bubbling air for 4 h was analyzed by reverse-phase HPLC as shown in Figure 3. Fractions at 16.5 and 17.4 min were assigned to unreacted pheophorbide *a* methyl ester (**1**) and the 13^2-stereoisomer of **1**, namely pheophorbide *a′* methyl ester, respectively. A new fraction, which had Soret and Q_y bands at 407 and 697 nm, respectively, in the HPLC eluent, appeared at 28.5 min (denoted by # in Figure 3). Other fractions at 10.5 and 32.3 min exhibited Q_y absorption bands around 665 nm. Therefore, the compound eluted at 28.5 min was the origin of the 700-nm absorption band formed by incubation of **1** with TiO_2 particles.

The 700-nm absorbing compound, which was detected at 28.5 min in the chromatogram in Figure 3, was isolated by reverse-phase HPLC. The purified compound was characterized by means of UV–vis, NMR, ESI-MS, and FT-IR measurements.[22] In addition, the spectroscopic data of this product were compared with those of purpurin-18 methyl ester (**2**) (Figure 1B) that was conventionally synthesized under an alkaline condition with molecular oxygen according to previous reports.[23–25]

The compound purified from the supernatant of **1** after treatment with TiO_2 particles exhibited Soret and Q_y bands at 411 and 700 nm, respectively, in CH_2Cl_2. The Q_y band was red-shifted by 33 nm compared with **1**, and was characteristic of purpurin-18-type pigments, which had a six-membered anhydride exo-ring instead of an original five-membered exo-ring in **1**. This compound showed the molecular-ion peak at *m*/*z* 579.4 in the ESI-MS,[22] which was identical to the molecular weight of purpurin-18 methyl ester. In the ^1H NMR spectrum of the purified compound, two singlet peaks at 6.28 and 3.88 ppm, which were assigned to protons at the 13^2-position (1H) and in the 13^4-methoxycabonyl group (3H), respectively, of original **1**, disappeared (Figure S1).[22] All the signals in ^1H and ^{13}C NMR spectra of the purified compound corresponded with those of purpurin-18 methyl ester (**2**) by conventional synthesis.[22] Figure 4 shows expanded FT-IR spectra of the purified compound and the synthesized **2** as well as pheophorbide *a* methyl ester (**1**) in the wavenumber region between 1500 and 1850 cm^{-1}. The purified compound exhibited no stretching vibrational peak of the 13^1-carbonyl group, which was clearly detected at 1701 cm^{-1} in the FT-IR spectrum of **1**.[26] New vibrational bands were observed at 1713 and 1730 cm^{-1} in the IR spectrum of the purified compound instead. These bands were identical to those of the synthesized **2**, and were ascribable to the anhydride group of purpurin-18 type pigments. The vibrational band at 1603 cm^{-1}, which was assigned to a skeletal vibration characteristic of the chlorin macrocycle, of the purified compound was present at the same position as that of the synthesized **2**, and was shifted to lower wavenumber than that of **1** at 1617 cm^{-1}. The vibrational stretching band of 17^3-carbonyl group was preserved at 1744 cm^{-1} in the spectrum of the purified compound after incubation of **1** with TiO_2 particles. All the vibrational bands of the purified compounds were the same as those of the synthesized **2** (Figure S3).[22] These characterizations revealed that the new compound formed by treatment of **1** with TiO_2 particles was puruprin-18 methyl ester.

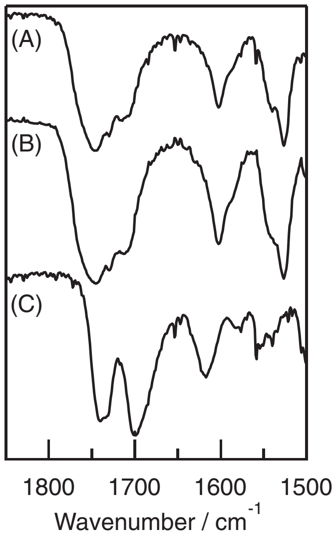

Figure 4. FT-IR spectra of the 700-nm absorbing compound purified from products after incubation of pheophorbide *a* methyl ester (**1**) with TiO_2 particles in CH_2Cl_2 by bubbling air (A), synthesized purpurin-18 methyl ester (**2**) (B), and pheophorbide *a* methyl ester (**1**) (C) in the region between 1500 and 1850 cm^{-1}.

The conversion efficiency from pheophorbide *a* methyl ester (**1**) to purpurin-18 methyl ester (**2**) under the present conditions for 4 h was estimated to be 32% (the average of three independent measurements). This value was smaller than the overall yield from **1** to **2** (50%) reported by Lee et al.[25] In the present reaction, CH_2Cl_2 was appropriate compared with other solvents such as methanol, which was used as a cosolvent

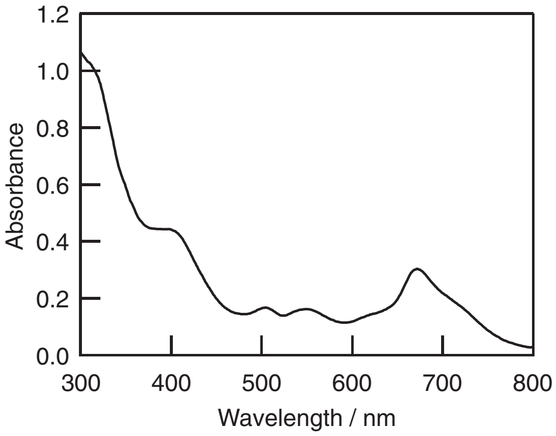

Figure 5. Visible absorption spectra of TiO_2 particles isolated from a CH_2Cl_2 suspension of pheophorbide *a* methyl ester (**1**).

in conventional synthesis of purpurin-18.[23–25] Reuse of TiO_2 particles decreased the conversion efficiency from **1** to **2** in this reaction (data not shown), probably because the active surface of TiO_2 particles was partially covered by adsorbed pigments. The amount of **1** used in this reaction was smaller than that in conventional synthesis.[23–25] Further studies will be required to increase the yield of **2** and the reaction scale by this method.

TiO_2 particles were collected from a CH_2Cl_2 suspension of **1** and TiO_2 particles, which was incubated for 4 h in the dark, by filtration, and washed with CH_2Cl_2. Figure 5 shows visible absorption spectra of TiO_2 particles after the incubation. The intense absorption band, which was ascribed to the Q_y band of adsorbed **1**, was observed at 672 nm. The Q_y band of **1** on TiO_2 particles was shifted to longer wavelength by 5 nm than **1** in CH_2Cl_2. Additionally, a new absorption band around 710 nm appeared, suggesting that **1** on TiO_2 particles was partially converted to purpurin-18 methyl ester.

To summarize, conversion of pheophorbide *a* methyl ester (**1**) to purpurin-18 methyl ester (**2**) by contact with TiO_2 particles in the presence of molecular oxygen was reported for the first time. The present one-step conversion from **1** to **2** under the mild condition is advantageous in conventional synthesis of purpurin-18 derivatives, in which hydrolysis of the 17-ester group takes place inevitably under strong alkaline conditions.[23–25] Investigation of a detailed reaction mechanism is now in progress. Such conversion will be useful for construction of DSSCs using Chl derivatives as photosensitizers[27] as well as development of facile synthesis of purpurin-18 derivatives, which attract considerable interest as near-infrared absorbing dyes.

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