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Photochemical Hole Burning of Tetraphenylporphine Glycosides

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Glycosilated tetraphenylporphine (TPP) were studied by photochemical hole burning (PHB) spectroscopy. A lactosylated TPP / poly(vinyl alcohol) shows excellent thermal stability against cyclic annealing, suggesting that the interaction between the lactosylated TPP and the matrix suppresses irreversible structural relaxation by forming hydrogen bonds.

Oligosaccharide chains covalently bound to the cell surface play a very important role in cell-cell and cell-matrix recognition processes.[1,2] A variety of glycosides have been synthesized in order to search for new advanced materials. Porphyrin glycosides were synthesized as a new class of water-soluble porphyrins.[3] Steric hindrance of the nonionizable glycosyl substituents also contributes to protecting the faces of the porphyrins and preventing the aggregation of the porphyrins.

Photochemical hole burning (PHB) is a fascinating method not only for application to optical frequency-domain information storage but also for scientific research on solid materials.[4,5] It enables us to obtain information on the local environment of chromophores in solids. In the present work we synthesized 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (TPP) glycosides with xylosyl or lactosyl groups on to the ortho, meta, or para position of meso-phenyl groups. The interaction between the TPP glycosides and matrices are studied by PHB spectroscopy. It has become apparent that the glycosyl groups would suppress thermal structural relaxation of the system by forming hydrogen bonds.

The TPP and 5,10,15,20-tetra(4-sulfophenyl)-21*H*,23*H*-porphine (TPPS(H)) were purchased from Wako Pure Chemical Industries, ltd. Tetrasodium 4',4'',4''',4''''-(5,10,15,20-tetraphenyl-21*H*,23*H*-porphine)-tetrasulfate (TPPS) was obtained by neutralization of TPPS(H) with sodium hydroxide. The TPP glycosides were synthesized according to the literature[3] with some modifications.[6] The chemical structure and the abbreviations of the porphyrins are shown in Fig.1. The polymers used as matrices are poly(methyl methacrylate) (PMMA), phenoxy resin(PhR), and poly(vinyl alcohol) (PVA). PMMA and PVA were purchased from Wako Pure Chemical Industries. ltd., and PhR was from Union Carbide Japan.

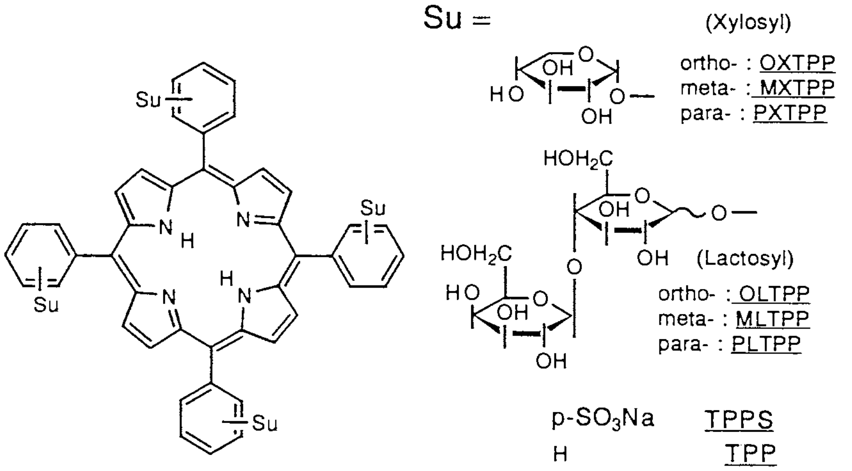

Fig.1. The chemical structure and the abbreviations of the porphyrins.

PMMA and PhR were purified by reprecipitation. The PHB samples were prepared with solvent cast method. Some samples were hot-pressed in addition to the casting process. The details of the sample preparation were depicted elsewhere.[7)]

The apparatus used for PHB measurements is the same one used in the previous work.[7)] Each samples was set in a cryostat with a closed-cycle helium refrigerator (Sumitomojuki, SRD204) and cooled to 20 K. A dye laser (Coherent, CR699-01) with DCM dye was used for hole formation. The dye laser was pumped with a cw argon ion laser (Coherent, Innova 70). The hole spectra were measured as transmission spectra with a one meter monochromator (Jasco, CT-100C), a photomultiplier (Hamamatsu, R943-02), and a lock-in amplifier (Jasco, LA-126W).

Typical hole profiles of PLTPP/PVA film during dye laser irradiation at 20 K are shown in Fig.2. The quantum efficiency for hole formation, Φ_{PHB}, was calculated by using the following equation (1),[7,8)]

$$\Phi_{PHB} = \{-(dA/dt)_{t=0}\} / \{10^3 I_0 (1-10^{-A_0}) \varepsilon R\} \qquad (1)$$

where A is time-varying absorbance, A_0 is the absorbance before irradiation, I_0 is the incident laser intensity given in einstein cm^{-2} s^{-1}, ε is the molar extinction coefficient for inhomogeneous line profile at the hole burning wavelength and temperature, and $R = \Delta\omega_i / \Delta\omega_{h,t=0}$ is the reciprocal

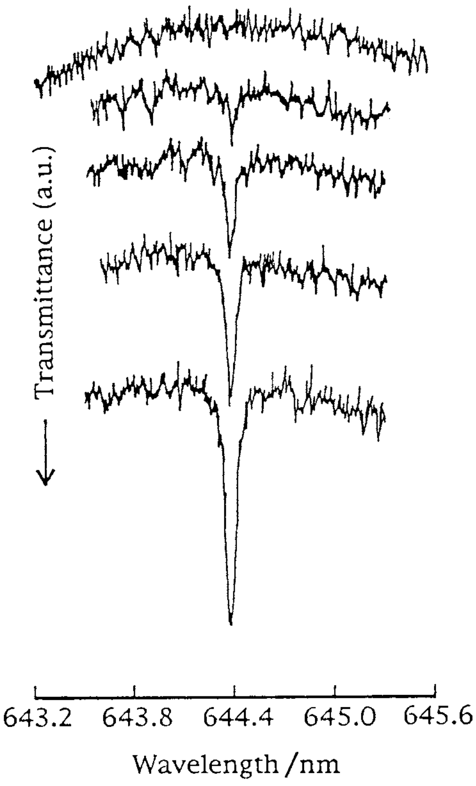

Fig.2. Hole profile change of PLTPP / PVA during dye laser irradiation at 20 K. Irradiation dose is 4.4 x 10^{-4} J cm^{-2} s^{-1}, irradiation times are 0, 1, 3, 5, and 10 s, from top to bottom.

initial ratio of a hole width, $\Delta\omega_{h,t=0}$, to an inhomogeneous line width, $\Delta\omega_{i}$.

Cycle annealing experiments were performed as follows: the sample was cooled to 20 K and irradiated by the laser light in order to burn a hole. The transmission spectrum was measured and then the temperature of the system was elevated and annealed. After the annealing for 20 min the sample was cooled to the initial hole burning temperature, 20 K, and a hole profile was measured again. This temperature cycle was repeated several times with stepwise raising of the elevated temperatures. The spectral change of the holes was evaluated from the hole area.

Table 1. The values of Φ_{PHB} and $\Delta\omega_{h,t=0}$ at 20 K. Spectral holes were burnt at the peak of Qx(0,0) band of each samples. ε is calculated from the absorbance at the peak of Qx(0,0) band of solution at room temperature.

Sample	Condition	$10^3\Phi_{PHB}$	$\Delta\omega_{h,t=0}$/cm^{-1}
PXTPP / PhR	Hot-Press	1.4±0.2	1.2
PXTPP / PMMA	Hot-Press	1.3±0.2	1.7
(PXTPP :	ε = 4.94×10^3 mol^{-1} L cm^{-1})		
MXTPP / PhR	Hot-Press	1.4±0.2	1.1
MXTPP / PMMA	Hot-Press	0.6±0.1	1.2
(MXTPP :	ε = 3.69×10^3 mol^{-1} L cm^{-1})		
OXTPP / PhR	Hot-Press	1.4±0.2	1.2
OXTPP / PMMA	Hot-Press	1.1±0.2	1.1
(OXTPP :	ε = 2.18×10^3 mol^{-1} L cm^{-1})		
PLTPP / PhR	Hot-Press	<0.1	1.1
PLTPP / PMMA	Hot-Press	0.9±0.1	1.7
PLTPP / PVA	Cast	2.2±0.4	1.6
MLTPP / PhR	Hot-Press	0.2±0.1	1.1
MLTPP / PVA	Cast	2.8±0.3	1.2
OLTPP / PhR	Hot-Press	0.3±0.1	1.2
OLTPP / PVA	Cast	1.5±0.2	1.2
TPP / PhR	Hot-Press	1.5±0.2	1.2
TPPS / PVA	Cast	4.4±1.0	1.2

The quantum efficiency for hole formation, Φ_{PHB}, is shown in Table 1. The values of Φ_{PHB} depend on the polymer matrix. For example, Φ_{PHB} of xylosylated TPP in PhR matrix is much higher than that in PMMA, and lactosylated TPP in PVA matrix is much more efficient for hole formation than that in PhR. It is known that Φ_{PHB} of TPP in various polymer matrices does not change much as long as the dye is well molecularly dispersed in the matrices.7) The difference due to the matrices would be caused by the solubility of the chromophores in the matrices. Generally low dispersivity of chromophores makes Φ_{PHB} much smaller. Little difference appears between ortho-, meta-, and para-substituted porphyrin as far as a series of each glycosilated substituent is concerned. By NMR measurement about 10% of protecting group, acyl group, may remain without elimination in the case of OLTPP. This may cause Φ_{PHB} of OLTPP/PVA to be reduced a little because of its low solubility in PVA matrix. The molar extinction coefficient, ε, is apparently affected by the position of the substituents. The xylosylated and lactosylated TPPs have the values of Φ_{PHB} approximately in the same order of magnitude as TPP has.

The results of the cycle annealing experiments are shown in Fig.3. It is well known so far that TPPS / PVA has the highest thermal stability of persistent spectral holes among dye / polymer systems.9,10) The thermal stability of TPPS / PVA is assumed to be due to rigidity of PVA matrix caused by high spatial density of hydroxyl groups, resulting in a large number of hydrogen bonds.10) PLTPP / PVA is superior to TPPS / PVA in thermal stability of a spectral hole. This suggests that the lactosyl groups of the chromophore would contribute to fixing the environment near the PLTPP molecules with plenty of hydroxyl groups. No improvement appears about thermal stability of a hole for PXTPP / PhR compared to TPP / PhR. This may result from the low spatial density of hydroxyl groups of the system. Both PVA and PhR contain one hydroxyl group per monomer unit, however, the monomer unit of PhR is much larger than that of PVA. Molecular weight of the monomer unit of each polymer is 284 (PhR), or 44 (PVA). The spatial density of hydroxyl groups of PXTPP / PhR is so low that the thermal stability of a spectral hole of PXTPP / PhR is as good as that of TPP / PhR.

It can be concluded that lactosylated TPP / PVA shows more excellent thermal stability of spectral holes than TPPS / PVA does. It suggests that hydroxyl groups of the chromophore interact with those of the matrix polymer, PVA, to suppress the thermal structural relaxation leading to hole filling.

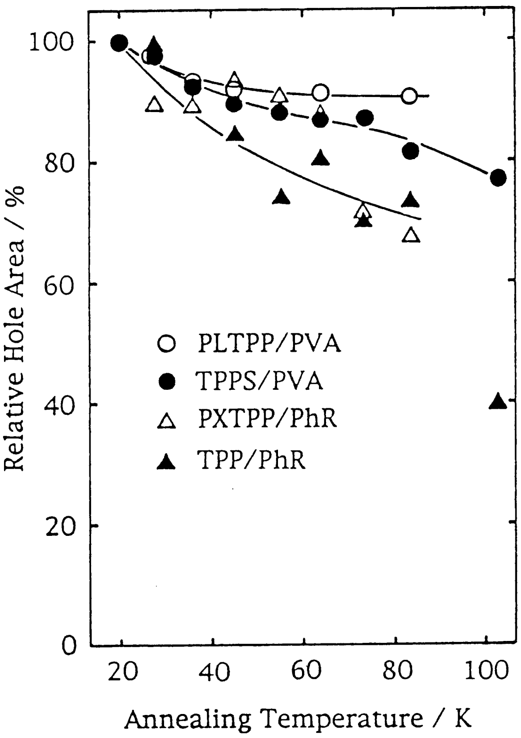

Fig.3. The results of the cycle annealing experiments. Spectral holes were burnt at 20 K and all of the spectral measurements were performed at 20 K.

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