Photochemical Hole Burning of Tetraphenylporphine Derivatives: Relationship between the Quantum Efficiency for Hole Formation and Chemical Structure of Tetraphenylporphine Derivatives

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The quantum efficiency for hole formation in photochemical hole burning (PHB) was measured for 10 derivatives of free base 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (TPP) at 20 K. The effect of the substituents on the quantum efficiency for hole formation does not follow the Hammett's rule contrary to a published report. The quantum efficiency for hole formation of the free base porphyrins is approximately 10^{-3} at 20 K. The lifetime of the lowest triplet state of the porphyrins was also measured at 77 K. There is no relation between the quantum efficiency for hole formation and the lifetime of the lowest triplet state.

Photochemical hole burning (PHB) has been attracting increasing attention in recent years. PHB has a possibility of being applied to a frequency-domain memory and of making a big improvement in the information-storage density.[3] On the other hand, PHB has also great advantage in scientific research. PHB can be utilized for getting rid of inhomogeneity in absorption spectra of chromophores dispersed in solids and realizing a high-resolution site-selective spectroscopy.[3,4]

The quantum efficiency for hole formation, Φ_{PHB}, is extremely low compared to those of common photochemical reactions, e.g., $\Phi_{PHB} = 2 \times 10^{-6}$ in case of quinizarin,[5] and $\Phi_{PHB} = (5 \pm 2) \times 10^{-3}$ for phthalocyanine.[6] The relationship between Φ_{PHB} and matrix polymers was studied in our laboratory,[7] by using free base 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (TPP) as a chromophore and various polymers as matrices. The highest value of Φ_{PHB} at 4 K, 1.1×10^{-3}, was observed for samples with a variety of organic polymers, i.e., poly(methyl methacrylate) (PMMA), phenoxy resin, polystyrene, and epoxy resin. The Φ_{PHB} obtained in these polymers are just the same and reproducible regardless of the matrices. This shows that the value of 1.1×10^{-3} in Φ_{PHB} reflects the essential limitation for spectral hole formation of TPP at 4 K. Probably it could not be expected that there exist other polymers which allow TPP to react much more efficiently than these polymers.

Sakoda[8] showed that deuterated free-base porphyrins are much less efficient for hole formation than hydrogenated free base porphyrins, supporting the idea that the rate-determining step would be the tautomerism of central protons of free-base porphyrins. The tautomerism of free base porphyrins is supposed to proceed via the lowest triplet state, T_1.[9] An effect of substituents of TPP derivatives on Φ_{PHB} was reported by Kishii,[10] insisting that increasing electron-donating ability of substituents on *meso*-phenyl groups in TPP improved the Φ_{PHB}, but only three porphyrins were examined in the report. In the study for finding out new chromophore molecules with high Φ_{PHB}, we tried reproducing the reported value of $\Phi_{PHB} = 3 \times 10^{-2}$ for 5,10,15,20-tetrakis(4-methoxyphenyl)-21*H*,23*H*-porphine (TMOPP),[10] but much smaller values were obtained. So we were obliged to examine chromophores with a wide variety of substituents in order to elucidate the effect of substituents of TPP derivatives on Φ_{PHB}. In the present paper Φ_{PHB} for 10 TPP derivatives are reported and discussed in relation to hole formation mechanism. The lifetime of the lowest triplet state of the porphyrins at 77 K are also presented.

Experimental Section

Chromophores. All the chromophores used in the present work are the derivatives of TPP. They are shown with the abbreviations in Figure 1. TPP and 5,10,15,20-tetrakis(4-sulfophenyl)-21*H*,23*H*-porphine (TPPS(H)) were purchased from Tokyo Kasei Kogyo Co., Ltd. TMOPP and 5,10,15,20-tetrakis-(2,3,4,5,6-pentafluorophenyl)-21*H*,23*H*-porphine (TFPP) were from Aldrich Chemical Co. Inc. 5,10,15,20-Tetrakis(4-carboxyphenyl)-21*H*,23*H*-porphine (TPPC(H)) and 5,10,15,20-tetrakis-(4-pyridyl)-21*H*,23*H*-porphine (TPyP) were from Wako Pure Chemical Ind. Ltd. 5,10,15,20-Tetrakis(4-methylphenyl)-21*H*,-23*H*-porphine (TMPP) and 5,10,15,20-tetrakis(4-ethylphenyl)-21*H*,23*H*-porphine (TEPP) were from Tokyo Chemical Corp. Four porphyrins, 5,10,15,20-tetrakis(4-chlorophenyl)-21*H*,23*H*-porphine (TChPP), 5,10,15,20-tetrakis(4-nitrophenyl)-21*H*,23*H*-porphine (TNPP), 5,10,15,20-tetrakis(4-cyanophenyl)-21*H*,23*H*-porphine (TCyPP), and TMOPP were synthesized according to

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[1] Research Laboratory, Nikon Corp.

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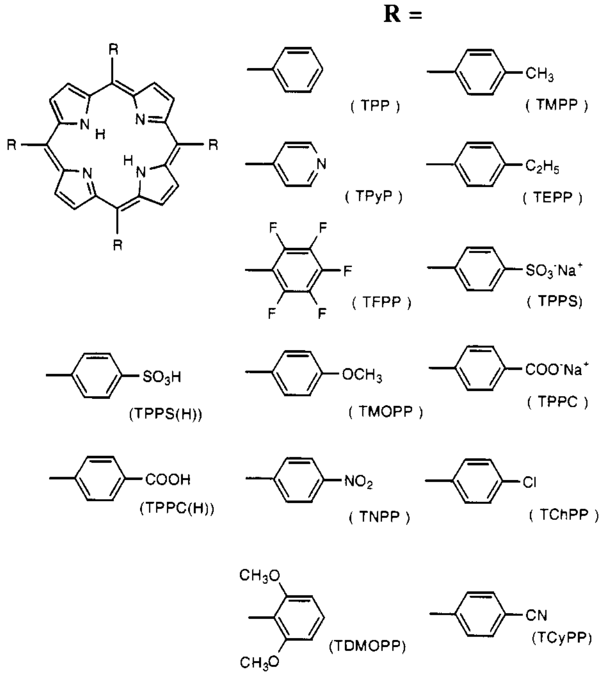

Figure 1. Abbreviations and structure of the porphyrins used as chromophores.

Thomas's method.[11] Tetrasodium 4′,4″,4‴,4⁗-(5,10,15,20-tetraphenyl-21*H*,23*H*-porphine)tetrasulfonate (TPPS) and tetrasodium 4′,4″,4‴,4⁗-(5,10,15,20-tetraphenyl-21*H*,23*H*-porphine)-tetracarboxylate (TPPC) were prepared by neutralization with sodium hydroxide from TPPS(H) and TPPC(H), respectively. Excessive sodium hydroxide was added to TPPS(H) in the present work.

Matrices. All of the matrices used are organic polymers, i.e., poly(methyl methacrylate) (PMMA), phenoxy resin (PhR), polystyrene (PS), poly(vinyl alcohol) (PVA), poly(sodium 4-styrylsulfonate) (PSS), and a fluorine-containing polymer (PVHT). PMMA was purchased from Wako Pure Chemical Ind. Ltd., and it was purified by reprecipitation. The PhR was from Union Carbide Japan, and it was purified by reprecipitation in the similar way to PMMA. PS is a commercial product named "Styron 693", which was supplied by Asahi Chemical Industry Co. Ltd. PSS was purchased from Aldrich Chemical Co. Inc. PVA was purchased from Wako Pure Chemical Ind. Ltd. PVHT was supplied by Central Glass Co. Ltd.

Samples. The PHB samples were prepared with solvent cast method. In addition to the evaporation, some samples were dried in a vacuum oven at about glass transition temperature (T_g) of the matrix polymer and were hot-pressed just above T_g with a pressing machine (Refinetech Co., MPO-110). The hot-pressing process was performed just above 1 kgf cm^{-2}. Finally sample disks with about 0.5-mm thickness were prepared.

PHB measurement. The apparatus used for PHB measurement is the same one used in the previous works[12] except the cryostat part. An outline of apparatus is shown in Figure 3. Each sample was set in a cryostat with a closed-cycle helium refrigerator (Sumitomojuki, SRD204) and cooled to 20 K. To attain good thermal contact, all the samples were sandwiched between two single-crystal sapphire plates (2 × 3 × 0.1 cm). A small amount of high vacuum grease (Toray Dow Corning Silicone Co.) was smeared on both sides of the samples and also on a part of the cold head which contacted with the sapphire plates. The temperature of the sample cannot be measured in situ because all the samples are sandwiched between the two sapphire plates. In our preliminary experiments the sample temperature was measured to be 20 K. Besides the hole widths for TPP obtained with the closed-cycle helium refrigerator are just the same within experimental errors as those measured at 20 K with a flow-type cryostat (Oxford, CF-1204). A dye laser (Coherent, CR699-01) was used for hole formation at the peak of $Q_x(0.0)$ band of each porphyrin. The dye compound used for the dye laser was DCM. The dye laser was pumped with a cw argon ion laser (Coherent, Innova70).

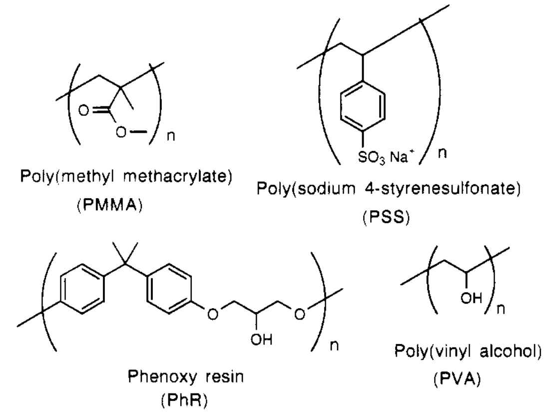

Figure 2. Abbreviations and structure of the polymers used as matrices.

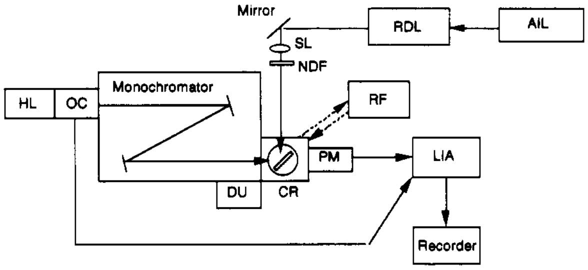

Figure 3. Apparatus for PHB measurement. HL: halogen lamp. OC: optical chopper. DU: driving unit for the grating. CR: cryostat. AIL: argon ion laser. RDL: ring dye laser. RF: refrigerator. LIA: lock-in amplifier. NDF: neutral density filter. SL: simple lens. PM: photomultiplier.

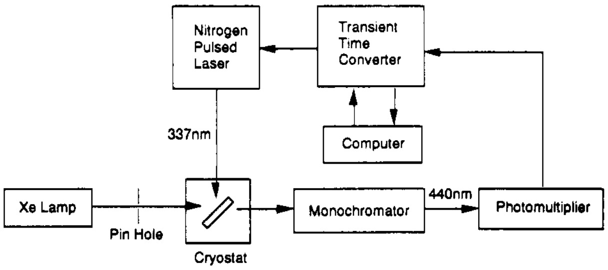

Figure 4. Outline of apparatus used for transient measurement of T–T absorption.

The hole spectra were measured as transmittance spectra with a 1-m monochromator (Jasco, CT-100C). A photomultiplier (Hamamatsu, R943-02) and a lock-in amplifier (Jasco, Model LA-126W) were used for hole spectra measurement.

We calculated the quantum efficiency for hole formation, Φ_{PHB}, by using eq 1,[5,12] where A is time-varying absorbance, A_0 is the

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

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 $R = \Delta\omega_i/\Delta\omega_h$ is the reciprocal initial ratio of a hole width, $\Delta\omega_h$, to an inhomogeneous line width, $\Delta\omega_i$.

Transient Measurements of T–T Absorption. The triplet lifetime of the prophyrins was calculated from the decay rate of T–T absorption. The outline of the apparatus is shown in Figure 4. The sample set in another cryostat (Oxford, DN-704) was cooled to the liquid nitrogen temperature. A pulsed nitrogen laser (Avco, C950B) as an exciting light at 337 nm, Xe lamp

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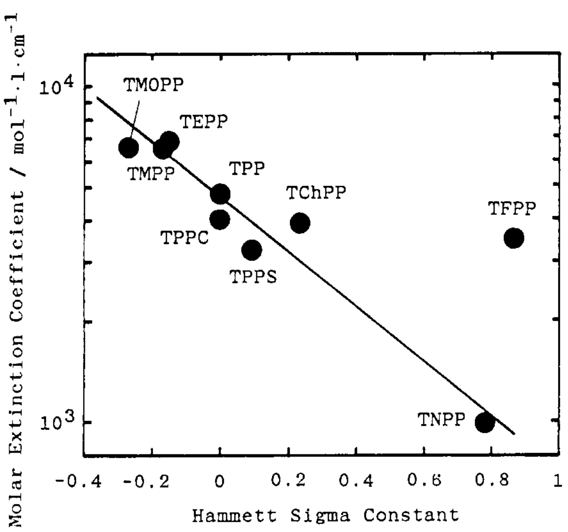

Figure 5. Hammett plot of molar extinction coefficients of the TPP derivatives in solutions: TMOPP and TNPP in chloroform; TMPP, TEPP, and TFPP in THF; TPP in benzene; TPPC and TPPS in water; TChPP in pyridine.[14]

(Hamamatsu, L-2195; 150 W) as a monitoring light source, monochromator (JASCO, CT10), photomultiplier (Hamamatsu, R374), and transient time converter (Riken Denshi, TCE-1000B) were used.

Monitoring light at 440 nm was steadily irradiated and N_2 pulsed laser at 337 nm was shot at intervals of several seconds.[13] Lifetime measurement was repeated more than ten times for sample and the data were integrated. The T_1 lifetime of the porphyrins, τ_T, was calculated from eq 2 with the least-squares

$$\mathrm{OD} = \log(I_0/I) = \epsilon[T_1]l = \epsilon l A \exp(-t/\tau_T) \qquad (2)$$

fitting method, where I_0 is the intensity of incident monitoring light, I is that of transmittance light, ϵ is the molar extinction coefficient of T–T absorption at 440 nm and 77 K, l is the light path length, and A is the preexponential factor.

Results and Discussion

Molar Extinction Coefficients of the Porphyrins. The values of molar extinction coefficients measured in solution are used for the basis of the calculation of Φ_{PHB}. The Hammett plot of the molar extinction coefficients of TPP derivatives at room temperature in solution give a straight line as is shown in Figure 5. The molar extinction coefficient of TChPP was reported to be 3930 mol^{-1} L cm^{-1}.[14] For TPP derivatives the peak wavelength and the ratio of the transition dipoles of the Q(0,0) (I and III peaks) to the Q(0,1) (II and IV peaks) bands are reported to be influenced by the substituents in accordance with the Hammett's correlation.[15] The molar extinction coefficient of TCyPP was reported to be 3400 mol^{-1} L cm^{-1} in pyridine.[16]

Since TFPP has ortho substituents on the phenyl groups, the total Hammett σ constant could not be calculated. In the report[10] the Hammett σ value of the ortho fluorine is assumed to be equal to that at the para position, +0.06. The value at the meta position is +0.34. Therefore the total Hammett σ constant for the five fluorines would be calculated $0.34 \times 2 + 0.06 \times 3 = +0.86$. The molar extinction coefficient of TFPP was measured to be 3500 mol^{-1} L cm^{-1} in the present work. This value, 3500 mol^{-1} L cm^{-1}, is far away from the fitted line in Figure 5, if the total Hammett σ value of +0.86 is adapted. In general free-base porphyrins have characteristic four absorption bands, Q bands, in the region of 500–700 nm. The TFPP has just three Q-band peaks,[17] contrary to the other porphyrins used in the present work. TFPP should have unique electronic states compared to the other TPP derivatives.

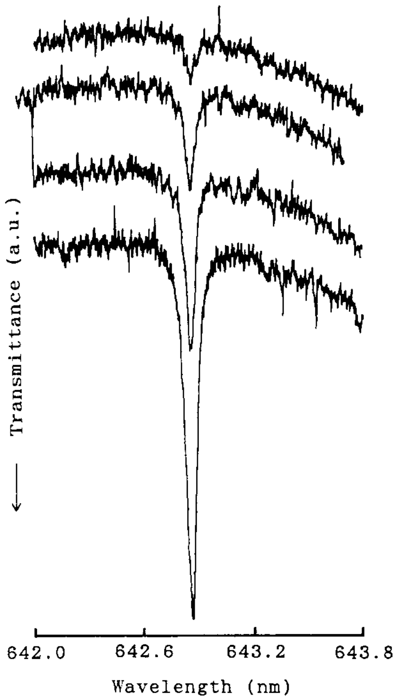

Figure 6. Hole profile change of TPP/PhR during dye laser irradiation at 20 K. Irradiation dose is 4.4×10^{-4} J cm^{-2} s^{-1}, time is 3, 10, 30, and 60 s, respectively.

Table I. Hot-Pressing Effect on Quantum Efficiency for Hole Formation, Φ_{PHB}, and Hole Width, $\Delta\omega_h$, of TMOPP Samples at 4 or 20 K

sample	preparation	$10^4\Phi_{PHB}$	$\Delta\omega_h$/cm^{-1}
TMOPP/PMMA	hot-press	6.6 ± 1.0 (20 K)	1.7
		6.7 ± 1.0 (20 K)	2.2
		6.9 ± 1.0 (20 K)	1.8
TMOPP/PMMA	cast	2.1 ± 2.0 (20 K)	5.0
		1.0 ± 2.0 (20 K)	3.0
		4.7 ± 2.0 (20 K)	4.5
		1.0 ± 2.0 (20 K)	4.5
TMOPP/PhR	hot-press	6.1 ± 1.0 (20 K)	1.6
		11.4 ± 1.0 (4 K)	0.6

Influence of Sample Preparation Methods. At first the high-temperature evacuation and the hot-pressing process were applied in order to remove the residual solvent molecules completely. Typical changes in hole profiles during dye laser irradiation are shown in Figure 6. The quantum efficiency for hole formation, Φ_{PHB}, was calculated from the initial slope of time–hole depth curves with eq 1. It was found that the hot-pressing process does affect both Φ_{PHB} and the hole width (Tables I and II and Figures 7 and 8). The polymers for which the hot-pressing could be applied are PMMA and PhR. The hot-pressed samples show larger Φ_{PHB} and smaller hole width than the cast ones. The values of Φ_{PHB} for the hot-pressed samples are

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Table II. Quantum Efficiency for Hole Formation, $\Phi_{\rm PHB}$, and Hole Width, $\Delta\omega_{\rm h}$, of TPP Derivatives at 20 K

sample	preparation	$10^4\Phi_{\rm PHB}$	$\Delta\omega_{\rm h}$/cm^{-1}
TPP/PMMA	cast	3 ± 2	4.1
TPP/PMMA	hot-press	10 ± 1	1.8
TPP/PhR	cast	3 ± 2	4.3
TPP/PhR	hot-press	10 ± 1	1.3
TMOPP/PMMA	hot-press	7 ± 1	1.7
TMOPP/PMMA	cast	3 ± 2	4.3
TMOPP/PhR	hot-press	6 ± 1	1.6
TFPP/PMMA	cast	2 ± 1	3.7
TFPP/PMMA	hot-press	1 ± 0.5	1.8
TPPS/PVA	cast	18 ± 2	1.2
TPPS/PSS	cast	17 ± 2	1.1
TPPC/PVA	cast	13 ± 2	1.2
TPyP/PhR	hot-press	8 ± 2	1.8
TChPP/PMMA	hot-press	1 ± 0.5	2.7
TChPP/PhR	hot-press	5 ± 1	1.4
TCyPP/PhR	hot-press	14 ± 2	1.3
TMPP/PhR	hot-press	9 ± 1	1.5
TEPP/PhR	hot-press	5 ± 1	1.7
TEPP/PMMA	hot-press	2 ± 1	2.1

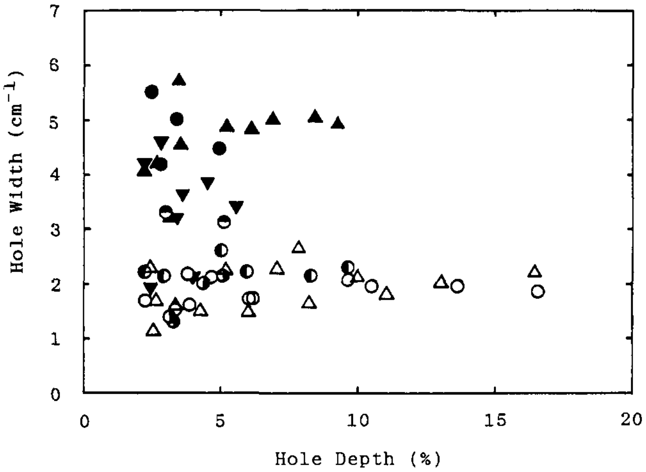

Figure 7. Hole widths vs hole depths of samples with PMMA as a matrix at 20 K. Hot-pressed samples are TPP (○), TMOPP (△), and TEPP (◐). Cast ones are TPP (●), TMOPP (▲), and TFPP (▼). TPP (⊖) was dried at T_g in vacuum.

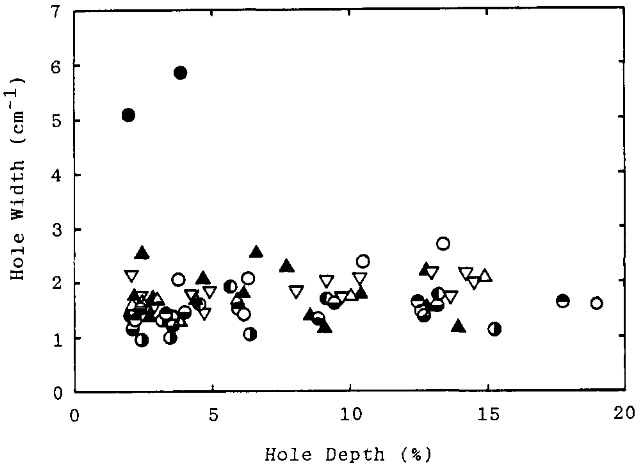

Figure 8. Hole widths vs hole depths of samples with PhR as a matrix at 20 K. Hot-pressed samples are TPP (○), TMOPP (◐), TEPP (▽), TChPP (◒), TCyPP (⊖), TDMOPP (◑), TPyP (▲), and TMPP (△). Cast one is TPP (●).

at least twice as large as those of the cast ones and the hole widths of the hot-pressed samples are half widths of the cast ones. As far as PMMA is concerned, the quantity and the nature of the residual solvent affect neither $\Phi_{\rm PHB}$ nor hole width. Heating and molding processes are believed to be the cause of the differences, because a sample being left at room temperature for 10 days and having little residual solvent shows a smaller $\Phi_{\rm PHB}$ and a wider hole width than the hot-pressed TPP samples, which is typical of the cast samples. This sample was proved to have very little residual solvent, because its heating above T_g in vacuo after PHB measurement showed no bubble formation. Since the lower $\Phi_{\rm PHB}$ and the wider hole width may be attributed to a deactivation pathway specific to the cast samples, the highest values of $\Phi_{\rm PHB}$ obtained for hot-pressed samples will be mainly discussed below.

Quantum Efficiency for Hole Formation. Various experiments were performed as is typically shown in Table I for the case of TMOPP. The TMOPP did not show such a high quantum efficiency as was reported in the letter,[10] where it was claimed that the $\Phi_{\rm PHB}$ of TMOPP is 7.5 times higher than that of TPP. It should be noted that the $\Phi_{\rm PHB}$ for TMOPP is not so high, even though a sample was prepared according to the Kishii's method, i.e., acetone was used as a solvent for casting, the PMMA was purchased from General Science Corp., and the sample was prepared without hot-pressing.[18] In general the hot-pressed samples with PMMA matrix is more efficient for hole formation than the cast ones. The hole width of the cast samples with PMMA matrix is about two times that of the hot-pressed samples with PMMA matrix. It should be concluded that TMOPP has the quantum efficiency for hole formation, 7×10^{-4} at 20 K, which is roughly the same as that of TPP. The values of $\Phi_{\rm PHB}$ for various TPP derivatives are summarized in Table II.

The $\Phi_{\rm PHB}$ of TFPP was obtained to be 2×10^{-4} at 20 K. This value is much higher than that in the report.[10] Because of the poor solubility of TFPP in PMMA, it was rather difficult for TFPP molecules to be dispersed perfectly in the samples. The $\Phi_{\rm PHB}$ of TFPP might be higher than 2×10^{-4} at 20 K, if a sample with molecularly dispersed TFPP is realized.[19] In the present work, it can be said that the $\Phi_{\rm PHB}$ of TFPP is not less than 2×10^{-4} at 20 K.

TPPS is the most efficient chromophore for hole formation in the present work, i.e., $\Phi_{\rm PHB} = 1.8 \times 10^{-3}$ at 20 K. Sakoda[20] claimed that TPPC/PSS is twice as *efficient for hole formation* as TPPC/PVA. But in the present work no difference between PSS and PVA matrices was found; TPPS/PVA exhibits $\Phi_{\rm PHB} = 1.8 \times 10^{-3}$ and TPPS/PSS shows $\Phi_{\rm PHB} = 1.7 \times 10^{-3}$. These two values in $\Phi_{\rm PHB}$ are regarded as just the same within experimental errors. TPPS is twice as efficient as TPP and shows narrower hole than TPP does. TPPC is a little more efficient for hole formation than TPP.

The TPyP samples were not in good condition owing to the poor solubility of TPyP. The absorption spectra of the samples show large scattering in the region on visible light. TPyP aggregation is believed to cause the scattering. They have, however, enough absorbance of the Q bands for PHB measurement. It is probably because some of the TPyP molecules in the samples aggregate and the others are molecularly dispersed. It was possible to measure the $\Phi_{\rm PHB}$ for TPyP, but the $\Phi_{\rm PHB}$ varied widely from sample to sample. Certainly there are some differences between the samples, TPyP would be approximately as efficient for hole formation as TPP.

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(20) Sakoda, K. *Prepr. Symp. Photochem.* **1990**, 519.

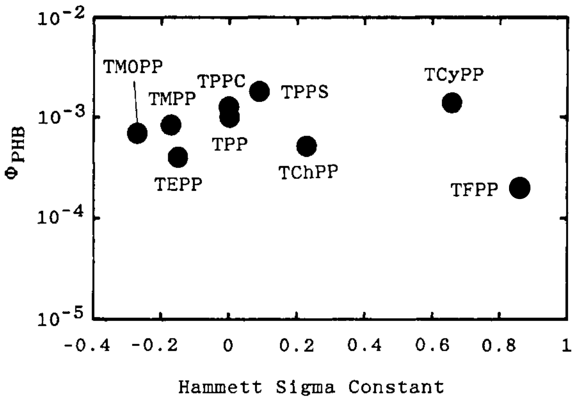

Figure 9. Hammett plot of the highest quantum efficiency for hole formation, Φ_{PHB}, of the TPP derivatives at 20 K.

The Φ_{PHB} of TCyPP, 1.4×10^{-3}, is a little bit larger than that of TPP. The hole width of the TCyPP sample is smaller than those for TPP samples. The smaller hole width might be attributed to the electron lone pairs of cyano groups in TCyPP. The interaction between the cyano groups of TCyPP and the hydroxyl groups of PhR matrix might depress the relaxation.

TChPP samples show a striking matrix effect on Φ_{PHB}. The TChPP/PhR system has a little bit smaller Φ_{PHB} than TPP samples, however, TChPP/PMMA samples show much smaller Φ_{PHB} than TChPP/PhR does. There are no differences between the absorption spectra of the samples in the visible region.

The Φ_{PHB} of TMPP, 9×10^{-4}, is almost the same as that of TPP. Probably it is because the similarity between hydrogen atom and methyl group at the para position of the phenyl groups of the porphyrins. In contrast to the similarity of the Φ_{PHB}, the molar extinction coefficient of TMPP is apparently larger than that of TPP at room temperature. It is certain that the methyl groups in TMPP do affect the electronic state of the porphine ring. But the substituent would have little influence on Φ_{PHB}.

The ethyl groups in TEPP reduce Φ_{PHB} less than a half that of TPP. The Hammett σ constant of the para ethyl group, −0.15, is almost the same as that of the para methyl group in TMPP, −0.17. The values of Φ_{PHB} are, however, different by a factor of about 2. It suggests that not only electronic inductive and resonant effects but also steric (or another) one affect Φ_{PHB}.

The highest values of Φ_{PHB} for each derivative of TPP are summarized in Figure 9. They differ from one another a little bit, and the differences do not correspond to the Hammett σ constants of substituents on *meso*-phenyl groups of TPP. These results contradict those of the report.[10] According to the report, the Φ_{PHB} of TMOPP, TPP, and TFPP should be 3×10^{-2}, 4×10^{-3}, and 2×10^{-5} at 4 K, respectively. The Φ_{PHB} at 4 K was also measured in the present work for TMOPP/PhR (hot-pressed). Its value of 1.1×10^{-3} is very close to that for TPP/PhR (hot-pressed) at 4 K (1.1×10^{-3}).[12] The temperature dependence of Φ_{PHB} for TMOPP/PhR below 30 K is supposed to be as small as that for TPP/PhR.[12] The Φ_{PHB} for TPPs with several substituent groups was also reported by Hala.[21] Our results in the present work is supported by their work.

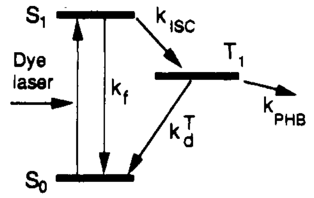

Figure 10. Energy level diagram for hole formation.

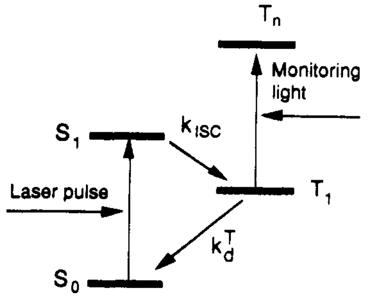

Figure 11. Energy diagram for lifetime measurement.

The NMR technique has given light upon the tautomerism of free base porphyrins in the ground state. It was found that there are no differences among the tautomerism rates of TPP derivatives in the ground state.[22] Their thermodynamic parameters are not affected by the chemical structure of their substituents. In contrast to the tautomerism in the ground state which proceeds with thermal excitation, the present results show that the rates for photochemical tautomerism of TPP derivatives may be affected just a little bit by their substituents.

Ample evidence exists that the phenyl ring and porphine planes are significantly noncoplanar in these molecules.[23] Angles of 60–85° between the phenyl ring and porphine planes were found in solids, and the angle of about 40° were calculated for TPP in solution.[24] It is suggested that the noncoplanar structure would prevent conjugation between the phenyl and porphine ring. Consequently the effect of the substituents at the phenyl groups on Φ_{PHB} may be greatly reduced.

The T_1 Lifetime of the Porphyrins. The energy level diagram for hole burning is shown in Figure 10.[9] The quantum efficiency for hole formation, Φ_{PHB}, would be written as follows:

$$\Phi_{PHB} = \{k_{ISC}/(k_{ISC} + k_f)\}\{k_{PHB}/(k^T{}_d + k_{PHB})\} \qquad (3)$$

Since Φ_{PHB} is much lower than that of intersystem crossing, k_{PHB} is negligible compared to $k^T{}_d$. It is well-known that the intersystem crossing, $S_1 \rightsquigarrow T_1$, is the dominant decay process of S_1 state in case of free base porphyrins and metalloporphyrins.[25] In the present work quantum efficiency for intersystem crossing, $\Phi_{ISC} = \{k_{ISC}/(k_{ISC} + k_f)\}$, is assumed to be independent of the substituents (0.85 for TPP).[26] Finally eq 3 would be transformed into eq 4, where τ_T is the lifetime of the T_1 state.

$$\Phi_{PHB} = \Phi_{ISC} k_{PHB}/k^T{}_d = \Phi_{ISC} k_{PHB} \tau_T \qquad (4)$$

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Table III. Lifetimes of the Lowest Triplet States, τ_T, of the TPP Derivatives at 77 K

sample	preparation	τ_T/ms
TPP/PhR	hot-press	6 ± 1
TPP/PhR	cast	6 ± 1
TPPS/PVA	cast	6 ± 1
TMOPP/PhR	hot-press	4 ± 1
TFPP/PMMA	cast	10 ± 1
TEPP/PhR	hot-press	5 ± 1
TPPC/PVA	cast	6 ± 1

The experimental results are shown in Table III. The values of τ_T for the porphyrins are similar to each other. The hot-pressing process does not affect the decay rate from the T_1 state, $k^T{}_d$. The largest τ_T was observed for TFPP, 10 ms. Φ_{PHB} for TFPP is, however, rather small than that of the other porphyrins. Consequently Φ_{PHB} is independent of τ_T. The differences in Φ_{PHB} should be attributed to the difference in the intrinsic rate coefficient, k_{PHB}.

Conclusion

The quantum efficiency for hole formation of 10 derivatives of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (TPP) was examined at 20 K. It is ascertained that the differences in quantum efficiency for hole formation among the porphyrins are rather small in contrast to those in the published report.[10] It is well-known that substituents on the phenyl groups of TPP have no influence on the thermodynamical parameters of tautomerism in the ground state.[22] In the case of PHB, it seems to exist a small substituent effect on Φ_{PHB}. Since the rate-determining step for hole formation is though to be the tautomerism of the inner protons, it would be suggested that the tautomerism in the excited state is affected to some extent by the substituents on the phenyl groups of the porphyrins, but it has no correlation with the Hammett σ values for the substituents on *meso*-phenyl groups. The lifetime of the lowest triplet state, from which the photochemical reaction for hole formation is thought to proceed, was also measured at 77 K. There is no relationship between the quantum efficiency for hole formation and the lifetime of the lowest triplet state of the derivatives of TPP.

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