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Journal of Photochemistry and Photobiology A: Chemistry 119 (1998) 53–60

Journal of Photochemistry and Photobiology A:Chemistry

Specific emission and quenching of photoexcited tetraphenylporphyrin derivatives incorporated in a Nafion film

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Received 30 March 1998; received in revised form 31 July 1998; accepted 31 August 1998

Abstract

According to the absorbance and fluorescence emission spectral changes, zinc ion in the ZnTPP (5,10,15,20-tetraphenylporphyrinatozinc (II)) was demonstrated to be replaced by two protons to form the free base tetraphenylporphyrin (H_2TPP) and further protonated to $[H_4TPP]^{2+}$ when the complex was incorporated into the hydrophobic fluorocarbon cluster in the Nafion alcoholic solution. This ion replacement and protonation took place very rapidly by incorporating the ZnTPP into a solid Nafion matrix. The photoexcited $[H_4TPP]^{2+}$ underwent a concentration quenching in the solid Nafion matrix. Although a dynamic quenching was involved (the second-order rate constant was $9.5 \times 10^7\ M^{-1}\ s^{-1}$), the static quenching was the major mechanism. Assuming that the probe molecules were distributed randomly in the Nafion matrix, the quenching distance between the center to center of the porphyrin molecules was calculated to be 1.6 nm. This diffusion coefficient was estimated to be $4.0 \times 10^{-8}\ cm^2\ s^{-1}$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tetraphenylporphyrin derivatives; Nafion; Concentration quenching; Static mechanism; Dynamic mechanism

1. Introduction

In the natural photosynthetic system, the porphyrin derivatives are known to form elaborate light-harvesting antenna complexes, which absorb low intensity sunlight and funnel energy to the reaction center. This energy transfer involves large number of chromophores, yet is extraordinary rapid over a long distance [1–4]. Because of the high quantum efficiency in both the energy transfer and the following charge separation processes, the porphyrin derivatives have been attracting a growing attention as a potential candidate for the photocatalysts to construct artificial photoenergy conversion systems [5–17]. A lot of researchers have focused attention on synthetic models to mimic the system, but it has been difficult to achieve high efficiency of the energy transfer and charge separation in the models similar to the natural systems [18–21].

Our final aim is to establish efficient catalysts for the artificial water photolysis to convert solar energy to chemical energy [22–25]. The issue has been studied by one of the present authors that some complexes can exhibit efficient activity for CO_2 reduction in an aqueous medium when they are incorporated into a hydrophobic polymer matrix [25]. Our recent studies have revealed that some metalloporphyrin and phthalocyanine complexes incorporated in polymer matrix can work as good catalysts for the electrochemical reduction of CO_2 to CO, or for the proton reduction to H_2 [26–29]. If they do act as catalysts in a water-photolysis system, their photophysical and photochemical behaviors in polymer matrix should be a crucial factor to affect the catalytic effect and reaction mechanism. The electron transfer by the electrochemical reduction of the tetraphenylporphyrin cobalt (CoTPP) in the polymer matrix was found to occur via a diffusion mechanism [30]. Because the electrochemical measurement is easily disturbed by some factors, especially the counterion migration to maintain the electron neutrality in the matrix, it is of interest to investigate the mobility of the porphyrin molecules in the polymer matrix by their emission and quenching processes in the photoexcited state [31–33].

Tetraphenylporphyrin derivatives have good solubility in organic solvents and their absorption and emission are characteristic in the visible region [34–38]. Recently, they were used as chromophores of self-assembly porphyrins or as large molecules linked with other molecules to study the

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1010-6030/98/$ – see front matter
PII: S1010-6030(98)00383-9

intramolecular energy or electron transfer [39–48]. Many of the studies have been carried out in organic solutions. One of the present authors has studied the intermolecular electron transfer from the zinc porphyrin to methyviologen (MV^{2+}) embedded in liposomes [49,50]. In this paper, the tetraphenylporphyrin derivatives are employed as a chromophore to study the emission and quenching process in a polymer matrix. Nafion is chosen as the polymer support because it is a sulfonated perfluoroalkyl polyanion known to be thermally stable, mechanically strong as well as chemically and biologically inert, and has been employed extensively as a support in various studies [51–53]. The properties of one of the derivatives in the matrix will be investigated to obtain better understanding of the ground state and the quenching of the excited molecule in the Nafion matrix.

2. Experiment

Nafion 117 solution (5.0 wt.% aliphatic alcohol), 5,10, 15,20-tetraphenylporphyrinatozinc (II) (ZnTPP) and meso-free base tetraphenylporphyrin (H_2TPP) compounds were purchased from Aldrich Chem. Co. Ltd. A Nafion alcoholic solution containing a known amount of ZnTPP (or H_2TPP) was diluted by butanol to 1.25 wt.% (density 0.8 g^{-1} cm^{-3}). 50 μl of this solution was cast on a non-emitting glass plate with 2.5 cm^2 area. After drying at room temperature under ambient conditions, the thickness of the film was about 1 μm (density 2.0 g^{-1} cm^{-3}) [54]. The concentration in the Nafion film was ranged from 0.025 to 0.10 M.

The visible absorption spectrum was measured with a Hitachi spectrophotometer U-150–20, and the emission spectrum with a Hitachi Fluorospectrophotometer F-2000. Emission decay was measured by a time-correlated single photon counting apparatus (Hitachi-Horiba Nanosecond Fluorometer 650–40) equipped with a 10 atm nitrogen lamp. The cell was deaerated by bubbling argon gas for 30 min before measurement. The fluorescence emission and decay of porphyrin derivatives in organic solution was measured by exciting with a Soret band and by monitoring through a Toshiba cutoff filter O-57. The glass plate coated with a porphyrin-containing Nafion film was immersed in a 0.10 M $NaClO_4$ (pH 1.2) aqueous solution that has been often used as an electrolyte solution to study electrochemical electron transfer of redox molecules in a Nafion film [54,55]. The plate was placed at a diagonal position in a quartz cell in the emission measurements. The emission and its decay were measured by exciting with a monochromatic light at the Soret band and by monitoring through an O-57 cutoff filter from the backside at right angle to the excitation light.

3. Results and discussion

The visible absorption spectrum of ZnTPP in benzene exhibited the Soret band at 420 nm (2.92 eV), Q(1, 0) band at 549 nm (2.24 eV), and Q(0,0) band at 587 nm (2.10 eV) as shown in Fig. 1. The molar absorption coefficient was obtained at low ZnTPP concentration scale in which $\varepsilon_{420} = 5.1 \times 10^4$ mol^{-1} m^2, $\varepsilon_{549} = 2.1 \times 10^3$ mol^{-1} m^2, and $\varepsilon_{587} = 3.4 \times 10^2$ mol^{-1} m^2. Its fluorescence emission spectrum showed two bands at 610 nm (Q(0,0)) and at 660 nm (Q(0,1)) (inset of Fig. 1). These spectra agrees with those reported by Longo, et al. [34,35]. The emission decay at 610 nm and 660 nm was monitored separately through Toshiba interference filters of KL-60 and KL-68. Both the decay curves can be well analyzed by a single-exponential function. The lifetime at 610 nm was estimated to be 1.90 ns and the lifetime at 660 nm 2.02 ns.

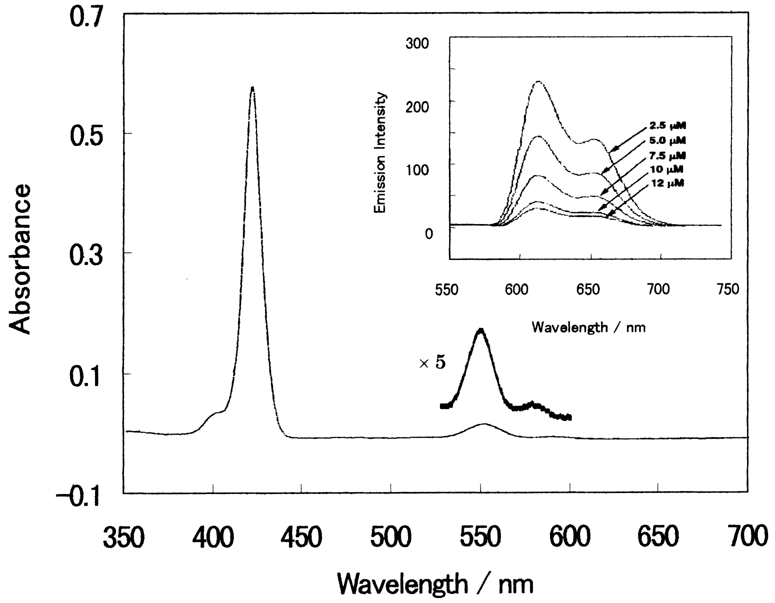

Fig. 1. Visible absorption spectrum of 1.2 μM ZnTPP in benzene solution in 1 cm quartz cell. The inset represents the fluorescence emission spectrum.

Table 1
Spectral data of the absorption and fluorescence emission by the tetraphenylprophyrin derivatives in various mediums

No.	Compound	State	Absorption (nm)					Emission (nm)			Color
			Soret band	Q band							
1	ZnTPP in benzene	Liquid	420		549	587		610	660		Purple
	ZnTPP in butanol	Liquid	422		548	588		610	660		Purple
3	ZnTPP in DMF	Liquid	424		558	598		610	660		Purple
4	H_2TPP in benzene	Liquid	418	514	548	602	650		670	714	Reddish
5	H_2TPP in Nafion butanolic solution $[H_4TPP]^{2+}$)[a]	Liquid	434			605	650		680		Green
6	ZnTPP in Nafion butanolic solution (fresh)	Liquid	422		557	596		610	662		Purple
7	ZnTPP in Nafion butanolic solution (150 days, $[H_4TPP]^{2+}$)	Liquid	434			606	655		678		Green
8	ZnTPP in solid Nafion matrix ($[H_4TPP]^{2+}$)	Solid	435			604	650		670		Green
9	(7) diluted 10 times with DMF (H_2TPP)	Liquid	417	514	548	590	646		660	712	Reddish
10	(5) diluted 10 times with DMF (H_2TPP)	Liquid	418	514	548	590	646		660	712	Reddish

[a] Absorption spectrum of $[H_4TPP]^{2+}$ in benzene/HCl solution at room temperature shows Q(1,0) band at 608 nm and Q(0,0) band at 685 nm according to [57].

The absorption and emission spectra of ZnTPP in the alcoholic solution were similar to those in benzene as shown in Table 1. The spectra were not influenced obviously when the Nafion was freshly dissolved, but changed gradually with time. After 150 days, its color changed from purple to green. In the absorption spectrum, the Soret band was red-shifted to 434 nm while the Q(1,0) band was at 606 nm and the Q(0,0) at 655 nm (Fig. 2). Only one emission band was observed at 678 nm. The green solution became reddish when diluted 10 times with *N*,*N*-dimethylforamide (DMF). The Soret band was blue-shifted to 417 nm while the Q bands were split into four bands at 514, 548, 590, and 646 nm (Fig. 3). Two emission bands were observed at 660 and 712 nm (Table 1). The absorption and emission spectra after keeping 150 days are very close to those of $[H_4TPP]^{2+}$, and its diluted solution (10 times by DMF) with the free base H_2TPP [56,57]. It is suggesting that the zinc ion in the ZnTPP complex was replaced by two protons to form freebase porphyrin H_2TPP and then further protonated to product $[H_4TPP]^{2+}$ in the Nafion alcoholic solution as follows,

$$\text{ZnTPP (purple)} \xrightarrow[\text{ion replacement}]{+2H^+} H_2\text{TPP (reddish)} \xrightarrow[\text{protonation}]{+2H^+} [H_4\text{TPP}]^{2+} \text{ (green)}$$

where the pK_a of H_2TPP is 4.0 [57]. The addition of DMF decreased the proton concentration in the solution so that the $[H_4TPP]^{2+}$ turned back to H_2TPP.

To demonstrate the core replacement reaction, H_2TPP was used as probe. The H_2TPP benzene solution is reddish colored, whose Sort band of absorption spectrum is at

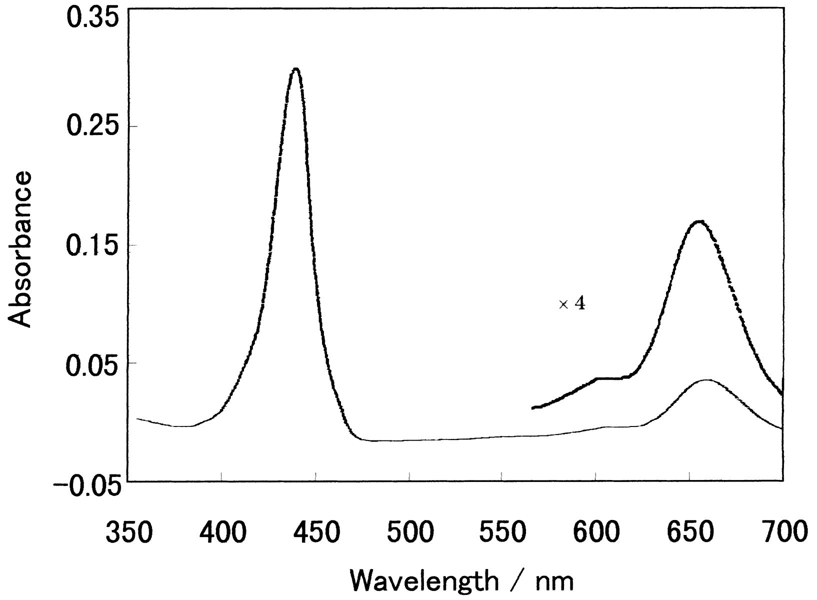

Fig. 2. Visible absorption spectrum of 12 μM porphyrin in Nafion micellae butanol solution reserved for 150 days in 2 mm quartz cell.

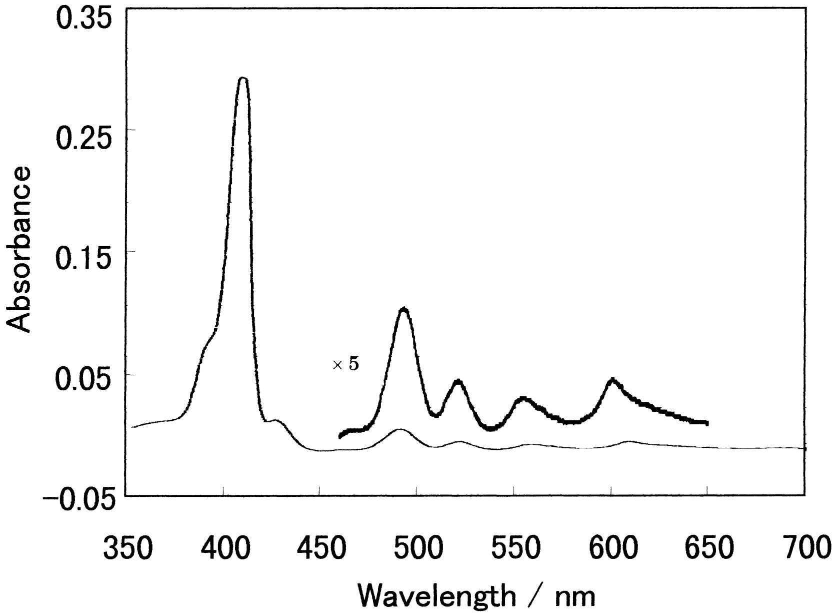

Fig. 3. Visible absorption spectrum of the 10 times diluted solution of Fig. 2 with DMF in 1 cm quartz cell.

418 nm. The Q(0,0) band splits into $Q_x(0,0)$ and $Q_y(0,0)$, and each band has a vibronic overtone $Q_x(1,0)$ and Q_y (1,0). The four bands are at 514, 548, 620, and 650 nm. The emission bands were at 670 and 714 nm. The Nafion alcoholic solution containing H_2TPP was green, and the Soret band was at 434 nm. The Q(1,0) and Q(0,0) bands were at 605 and 650 nm. The emission peak was single at 680 nm. When the H_2TPP Nafion alcoholic solution was diluted 10 times with DMF, the Soret band was blue-shifted to 418 nm and the Q bands were split to four bands at 514, 548, 590, and 646 nm. The emission spectrum showed two bands at 660 and 712 nm. Because the spectrum of the ZnTPP in the Nafion alcoholic solution after keeping for a long time agrees with that of $[H_4TPP]^{2+}$, and that its diluted solution (10 times by DMF) with that of H_2TPP, it is concluded that the ion replacement reaction takes place in the Nafion alcoholic solution.

Since the ZnTPP is not soluble in water, the ion replacement and the protonation cannot take place without the Nafion. With the strong hydrophobic fluorocarbon chains and the strong hydrophilic sulfonate groups, Nafion is expected to exist as a kind of micelle in an alcoholic solution where the fluorocarbon chain would form a hydrophobic cluster. This was supported by the fact that no porphyrin was precipitated even if a Nafion butanolic solution was diluted 10 times by methanol/water mixture solvent. The position of absorbance or emission bands was not influenced obviously by diluting. As an electron acceptor [24,25,57], methylviologen (MV^{2+}) could not quench the excited porphyrin molecule in a fresh Nafion alcoholic solution indicating that all the hydrophobic ZnTPP molecules were incorporated into the hydrophobic cluster of the Nafion and separated from the MV^{2+} in the alcoholic solution.

The color change from purple to green was very rapid when a solid Nafion[porphyrin] film was formed by casting a fresh ZnTPP Nafion alcoholic solution on a plate. The absorption and the emission spectra of this film were close to those of the ZnTPP Nafion alcoholic solution kept for 150 days. It means that the zinc replacement and protonation of ZnTPP in the solid Nafion matrix are much faster than those in the Nafion alcoholic solution. Considering that the ion replacement and protonation proceed by the sulfonic acid groups on the Nafion, the different reaction rate could be principally ascribed to the different microscopic environment in the Nafion alcoholic solution and the dry matrix. When dissolved in the Nafion alcoholic solution, the ZnTPP was expected to localize in the hydrophobic cluster of the Nafion so that they have lesser chance to contact with the hydrophilic sulfonic groups, and the reaction must be slow. However, because of the relatively loose packing of the solid Nafion morphology and undistinguished separation of hydrophilic/hydrophobic region under dry condition [58,59], the possibility of the ZnTPP to contact with the sulfonic acid groups would be improved greatly so that the ion replacement and the protonation becomes much faster.

The absorption and emission spectra of the $[H_4TPP]^{2+}$ in the solid Nafion as shown in Fig. 4 are close to those to the $[H_4TPP]^{2+}$ in the Nafion alcoholic solution (Fig. 2). The Soret band is at 435 nm; the Q(1,0) band at 604 nm and Q(0,0) band at 650 nm. The molar absorption coefficient ε_{435} was 1.2×10^4 mol^{-1} m^2, ε_{604} 8.4×10^1 mol^{-1} m^2, and ε_{650} 1.8×10^3 mol^{-1} m^2. Only one fluorescence emission was observed at 670 nm (inset of Fig. 4). An example of the decay curve of the Nafion[porphyrin] film is shown in Fig. 5. The decay curve was analyzed satisfactorily by a single-exponential function, and the lifetime decreased with

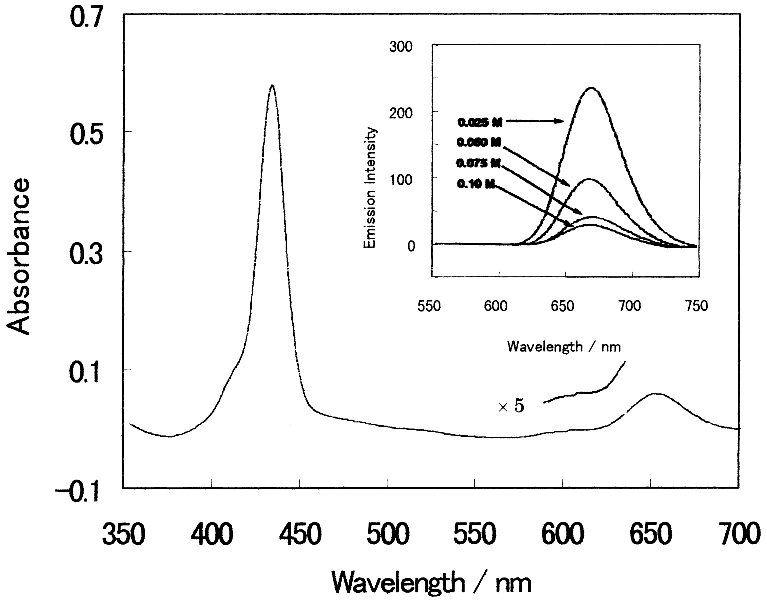

Fig. 4. Visible absorption spectra of 0.050 M porphyrin in the Nafion film with 1 μm thickness. The inset represents the fluorescence emission spectra.

increasing the probe concentration in Nafion as shown in the inset of Fig. 6. The values of χ^2 were from 1.37 to 1.67 which are given in the inset of Fig. 6. When double-exponential function or triple-exponential function was tried to fit the decay curve, only one lifetime component was obtained which is equal to that by the single-exponential function. The result indicates that the single-exponential function fits best for the decay curve.

The relative emission yield (Φ) of the excited porphyrin in the Nafion matrix was calculated according to Eq. (1),

$$\Phi = \frac{i}{1 - 10^{-\mathrm{Abs}}} \qquad (1)$$

where i is the relative emission intensity and Abs is the absorbance at 430 nm. The plot of Φ against the probe concentration in a Nafion film is shown in Fig. 6. The

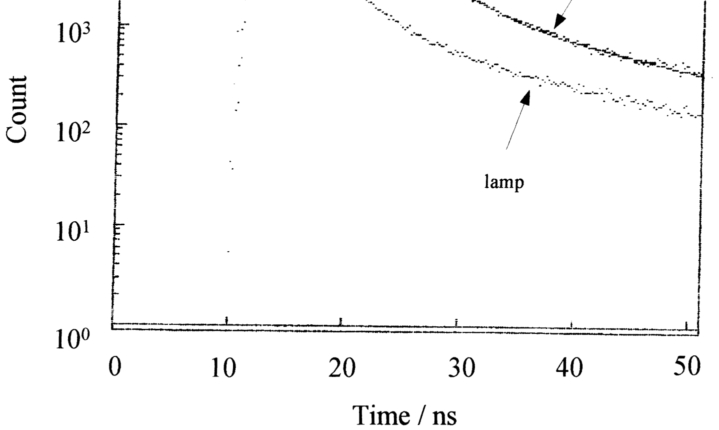

Fig. 5. Emission decay curve of photoexcited $[H_4TPP]^{2+}$ (0.050 M) in Nafion film.

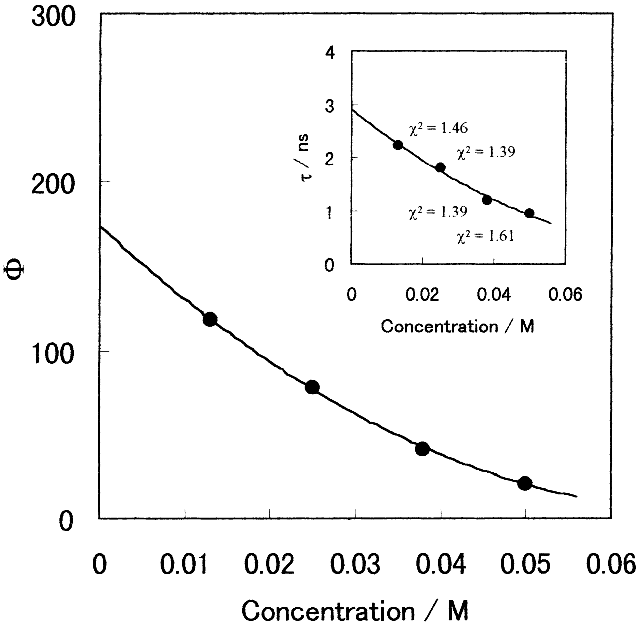

Fig. 6. The correlation between the relative emission yield (Φ) and the $[H_2TPP]^{2+}$ concentration in a Nafion film in contact with an aqueous electrolyte (0.10 M $NaClO_4$, pH 1.2). The inset represents dependence of the emission liftime (τ) on the $[H_4TPP]^{2+}$ concentration in the Nafion film showing also the χ^2 values.

emission intensity decreased with the probe concentration. The curve was extrapolated to zero concentration to obtain a hypothetical relative emission yield at infinite dilution Φ_0. The fluorescence emission intensity was also studied by changing the excitation light intensity with Toshiba Filters of ND-50 and ND-20 (Fig. 7). The result shows that the emission intensity increased as a first-order function with respect to the excitation light intensity, indicating that quenching between the excited states can be excluded. The excited probe must be quenched by a ground state molecule through a concentration quenching. The lifetime also decreased with increasing probe concentration as shown in the inset of Fig. 6. The curve is extrapolated to zero concentration to obtain the hypothetical luminescence lifetime at infinite dilution τ_0 where there is no concentration quenching. Stern–Volmer plots on the basis of the relative emission yield and the lifetime are given in Fig. 8.

A dynamic quenching takes place by diffusion and collision of molecules for which the quenching lifetime decrease with the increase of the quencher concentration. A dynamic quenching can be written as Eq. (2)[64],

$$\frac{\tau_0}{\tau} = 1 + k_{sv}c \qquad (2)$$

where c is the quencher concentration and k_{sv} is the Stern–Volmer constant. A static quenching takes place in a quenching sphere around an immobile luminescent probe for which the probe that contains the quencher in its quenching sphere does not emit al all. A combination of dynamic and static quenchings are also possible [60–63]. The result of Fig. 8 indicates that the major static quenching is accompanied by the minor dynamic quenching. When the probe concentration is 0.050 M for example, the static quenching efficiency is 12 times higher than the dynamic quenching efficiency. The small contribution by the dynamic quenching indicates that the porphyrin molecule can move slightly in the solid Nafion matrix. The second-order quenching rate constant k_{q2} ($=k_{sv}/\tau_0$) for the dynamic bimolecular mechanism was estimated to be 9.5×10^7 M^{-1} s^{-1} from the slope (k_{sv}) of the τ_0/τ plot against the probe concentration in the Nafion by the Eq. (2).

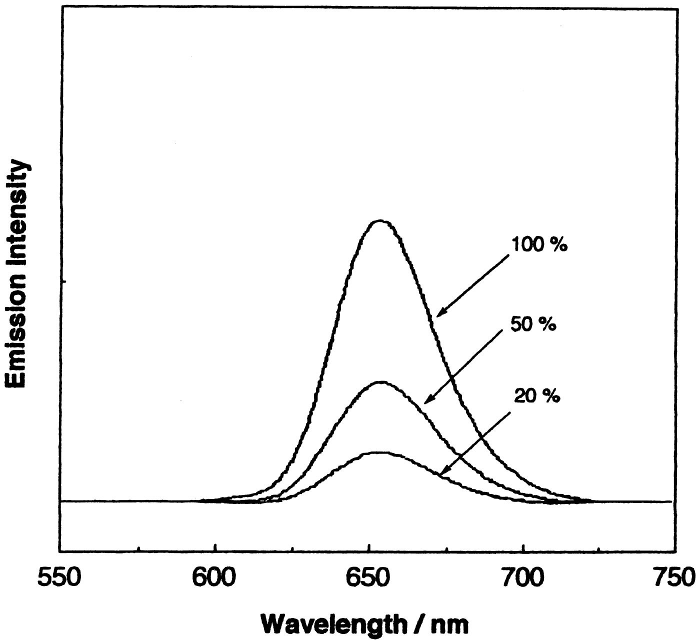

Fig. 7. The emission spectrum (0.10 M $[H_4TPP]^{2+}$) dependent on the relative excitation light intensity (100%, 50%, and 20%) in a Nafion matrix.

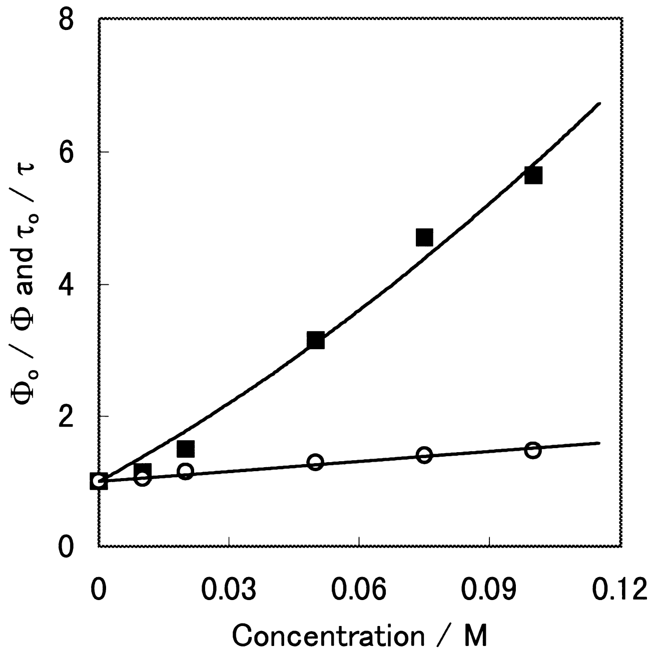

Fig. 8. Stern–Volmer plots of the photoexcited $[H_4TPP]^{2+}$ in the solid Nafion matrix on basis of the relative emission yield Φ_0/Φ (■) and the relative emission lifetime τ_0/τ (○).

Assuming that the probes are distributed randomly in the polymer matrix, the Perrin equations can be used to express the center-to-center quenching distance (R_0) for a static mechanism

$$\frac{\Phi_0}{\Phi} = \exp\left(\frac{4}{3}\pi R_0^3 N_A c \times 10^{-24}\right) \tag{3}$$

where N_A is the Avogadro's constant, and c is the probe concentration in the Nafion. Since the dynamic quenching contribution should also be considered, the present quenching should be expressed by Eq. (4).

$$\frac{\Phi_0}{\Phi} = \left(1 + k_{q2}\tau_0 c\right)\exp\left(\frac{4}{3}\pi R_0^3 N_A c \times 10^{-24}\right) \tag{4}$$

The radius of excluded volume of the porphyrin molecule (s) is introduced in Eq. (5).

$$\frac{\Phi_0}{\Phi} = \left(1 + k_{q2}\tau_0 c\right)\exp\left[\frac{4}{3}\pi\left(R_0^3 - s^3\right)N_A c \times 10^{-24}\right] \tag{5}$$

The $[H_4TPP]^{2+}$ was tentatively assumed as a sphere that has the same volume as a disk with 2.4 nm^2 area plane and 0.14 nm thickness [65], and the diameter of the hypothetical sphere of the $[H_4TPP]^{2+}$ was estimated as 0.86 nm, which was regarded as the contact distance (s). By using a non-linear least-square analysis method, the quenching distance R_0 for the static process was calculated to be 1.6 nm (center to center) from the Φ_0/Φ plots of Fig. 8 on the basis of Eq. (5).

If the dynamic bimolecular quenching in the Nafion film is a diffusion-limited process, the second-order quenching rate constant k_{q2} can be adopted to estimate the diffusion coefficient (D) via the Smoluchowski equation as Eq. (6) [31,66]

$$k_{q2} = \frac{p 4\pi R_0 D' N_A}{10^3} \tag{6}$$

where p is the encounter probability of two reactants resulting in quenching and D' is the sum of the diffusion coefficients of the ground and excited state probe. When assuming that each encounter leads to a quenching ($p = 1$), D' is calculated to be $8.0 \times 10^{-8}\ cm^2\ s^{-1}$. The diffusion coefficient of the excited state probe is $4.0 \times 10^{-8}\ cm^2\ s^{-1}$ when assuming that the values of the excited and ground state probes are the same.

Although the static quenching was the main mechanism, the probe can travel slightly during the excited state in the Nafion (lifetime is ca. 3.0 ns) and root mean square distance

$$R_t = \left(D'\tau\right)^{1/2} \tag{7}$$

for the travel is estimated by Einstein–Smoluchowski equation Eq. (7) to be 0.12 nm [52,60].

Acknowledgements

The authors acknowledge the Grant-in-Aid for the scientific research priority area of 'New Polymer and Their Nano-organized System' (No. 277/10126207) from Ministry of Education, Science, Sports and Culture.

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