

pH-Dependent Reversible Switching of Fluorescence of Water-Soluble Porphyrin Adsorbed on Mesoporous TiO_2 Film

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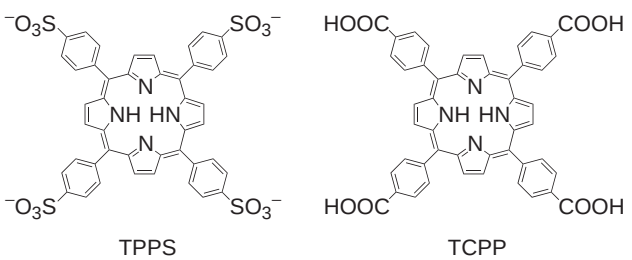
Changes of the fluorescence spectra of tetrakis(4-sulfonatophenyl)porphyrin (TPPS) and tetrakis(4-carboxyphenyl)porphyrin (TCPP) chemisorbed on TiO_2 film in pH-adjusted water have been investigated. TPPS on TiO_2 film in pH 6.5 water showed strong fluorescence, while it hardly emitted in pH 1.6 water, demonstrating a fluorescence switching with dramatic intensity changes in the TPPS–TiO_2 system. On the other hand, only small changes in the fluorescence were observed for TCPP adsorbed on TiO_2 instead of TPPS, although the changes were reversible. Fluorescence switching observed for TPPS and TCPP only in the adsorbed states on TiO_2 are discussed on the basis of quenching of the excitation energy caused by molecular arrangements on TiO_2 and photoinduced electron injection of excited porphyrin to TiO_2.

Porphyrin derivatives have attracted the attention of scientists due to not only natural systems such as photosynthetic antenna for light harvesting and heme proteins for storage or transportation of oxygen, but also their photophysical properties, such as a strong absorption in the visible region and fluorescence. Some porphyrin derivatives show high fluorescence quantum yields (10–30%),[1] allowing them to fabricate an efficient energy- or electron-transfer system.[2–5] The photophysical properties of porphyrins are significantly changed by protonation or metal coordination to the porphyrin core. Some protonated porphyrin derivatives are aggregative in an acidic medium. Particularly, diprotonated tetrakis(4-sulfonatophenyl)porphyrin (TPPS) (Fig. 1) in an acidic aqueous solution (pK_a = 4.8)[6] forms its J-aggregates[7–9] by electrostatic interaction between the positively charged porphyrin center and negatively charged peripheral sulfonic acid groups of neighboring TPPS, depending on the pH value and ion strength.[7–19] Since TPPS molecules readily form J-aggregates in acidic water, TPPS has been widely studied as a representative molecule among the derivatives of porphyrin, beside water-insoluble porphyrins forming J-aggregates.[20] The structure, aggregation number, and excited state of TPPS J-aggregates in acidic aqueous solution have been mainly reported so far.[7–19] The fluorescence decay time of 50 ps for J-aggregates in an aqueous solution has been reported, whereas approximately 3.9 ns has been reported for the diprotonated TPPS monomer.[11] The much shorter decay time of TPPS J-aggregates than that of the diprotonated monomer is related to exciton dynamics inducing the excitonic superradiance.[15]



TPPS TCPP

Fig. 1. Structures of TPPS and TCPP.

Molecules adsorbed chemically on metal oxide semiconductors have been intensively investigated, especially in the field of dye-sensitized nanocrystalline TiO_2 solar cells.[21–26] Femtosecond electron injection from a sensitizing dye to the TiO_2 conduction band through carboxyl groups has been observed by time-resolved spectroscopic measurements, indicating a quite efficient process.[27–31] Therefore, the fluorescence of sensitizing dye molecules chemisorbed on TiO_2 is generally quenched by the ultrafast electron injection. Electron-injection efficiency significantly depends on the strength of the interaction between anchoring groups and the surface of a metal oxide semiconductor. Hence, fluorescence intensity of a sensitizing dye can be controlled by selection of its anchoring groups.

TPPS can be adsorbed chemically on TiO_2 through its sulfo groups as anchoring groups.[32–39] Only a few studies related to the fluorescence of TPPS on mesoporous TiO_2 film have been reported.[32–34] Tamai et al. have reported the fluorescence decays of the protonated TPPS monomer and its J-aggregates on TiO_2 nanoparticles dispersed in TPPS aqueous solutions.[32] The paper mentioned that the fluorescence of both diprotonated monomer and J-aggregates adsorbed on TiO_2 nanoparticles was quenched by efficient electron injection from their excited singlet states into the conduction band of TiO_2 nanoparticles, resulting in short lifetimes of the excited states. However, they did not mention the contribution of energy annihilation occurring between TPPS molecules on the TiO_2 surface.

We have found that TPPS molecules chemisorbed on mesoporous TiO_2 film form molecular islands containing diprotonated monomers and J-aggregates in the islands by acidification of the surrounding water.[39] Furthermore, in this study, it has been demonstrated that the molecular arrangement of TPPS changes reversibly depending on the pH values of the

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surrounding water. Using nanocrystalline TiO_2 film enables us to change pH values alternately without aggregation of TiO_2 particles, whose isoelectric point is around pH 6.0. In the present work, we have focused on the changes of the relaxation processes of the excited state occurring in the system of the above molecular islands depending on pH. Then, the fluorescence of porphyrin adsorbed on TiO_2 film was investigated by selecting the anchoring group of porphyrin and changing the pH value of the surrounding water. In the present paper, it has been found that the fluorescence intensity of TPPS adsorbed on TiO_2 film is reversibly and drastically changed depending on the pH values of the surrounding water, indicating a fluorescence switching induced by pH-change. By comparison with the pH-dependent fluorescence spectra of tetrakis(4-carboxyphenyl)porphyrin (TCPP) (Fig. 1) on TiO_2 film, switching of the fluorescence has been found to be strongly dependent on the kind of anchoring group and molecular orientation. The switching mechanism is discussed on the basis of the changes of the relaxation processes of the excited state in relation with the changes of the arrangement of porphyrin molecules induced by changes of pH.

Experimental

Tetrakis(4-sulfonatophenyl)porphyrin (TPPS) and tetrakis(4-carboxyphenyl)porphyrin (TCPP) were purchased from Aldrich and TCI, respectively, and used without further purification. Transparent mesoporous TiO_2 film with a thickness of 2.6 μm was prepared by spreading a paste of colloidal TiO_2 nanoparticles (purchased from Solaronix) onto a fluorine-doped SnO_2 glass substrate. Then, the film was dried in air and sintered at 450 °C for 30 min. After cooling to room temperature, the mesoporous TiO_2 film was immersed in a TPPS-DMF solution (3.0×10^{-4} M) overnight. The TPPS-adsorbed TiO_2 film was washed with ethanol thoroughly and dried in air. TCPP-adsorbed TiO_2 film with almost the same absorbance at the B-band as TPPS-adsorbed TiO_2 film was prepared by adjusting the submersion time in a TCPP-DMF solution. After porphyrin-adsorbed TiO_2 films were placed into 1 cm quartz cells, the cells were filled with deionized water (pH 6.5) and acidic water (pH 1.6), alternately. Acidic water with a pH value of 1.6 was prepared by adding HClaq or HNO_3. As a reference, TPPS and TCPP aqueous solutions (5.65×10^{-6} M) having pH values of 9.8, 1.6, and 0.6 were prepared with NaOH for basification and HClaq or HNO_3 for acidification, respectively. In preparation of TCPP solutions, HClaq or HNO_3 was added after TCPP was completely dissolved in pH 9.8 water.

pH-Dependent absorption and fluorescence spectra of porphyrin-adsorbed TiO_2 film placed into quartz cells and porphyrin aqueous solutions were measured with a Hitachi U3300 spectrophotometer and Hitachi F4500 spectrofluorometer, respectively. All the measurements were carried out at room temperature.

Results and Discussion

pH-Dependent Reversible Spectral Changes of TPPS on TiO_2 Film. It has been reported that TPPS molecules chemisorbed on mesoporous TiO_2 film form J-aggregates in acidic water. Reversible arrangement changes of TPPS depending on pH value were observed by absorption measurements therein, indicating a dynamic behavior of molecular arrangement on the solid surface.[39] Figure 2 shows the absorption spectra of TPPS on TiO_2 film in surrounding water having an adjusted

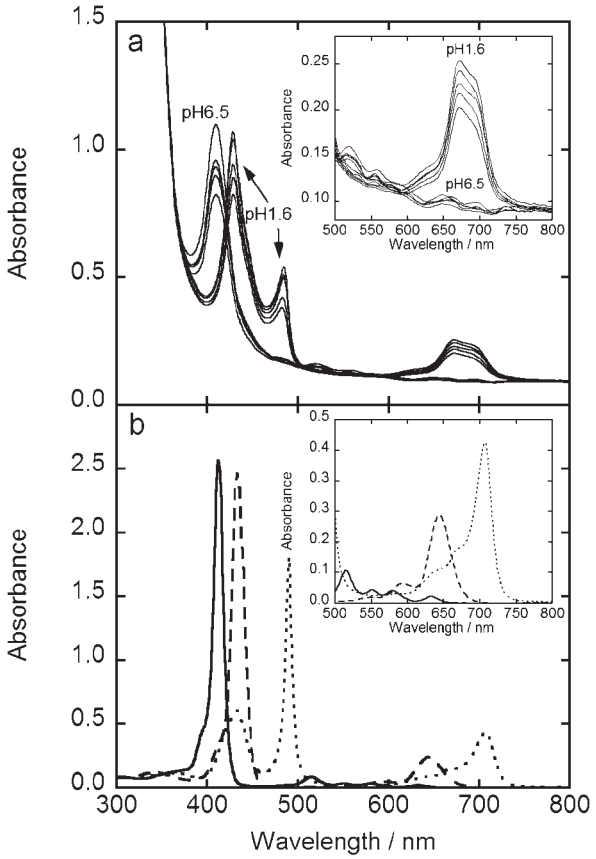

Fig. 2. Absorption spectra of (a) TPPS on TiO_2 film in waters having pH 6.5 water and pH 1.6 water and (b) TPPS in aqueous solutions (5.65×10^{-6} M) having different pH values; pH 9.8 solution (solid line), pH 1.6 solution (broken line), and pH 0.6 solution (dotted line). Absorption spectra of TPPS on TiO_2 film were measured with pH 6.5 and 1.6 waters, alternately. The insets of Fig. 2 indicate enlarged illustrations of Q-bands. pH Values of acidic water or solutions were controlled with HClaq.

pH and TPPS in aqueous solutions. Figure 2a indicates changes of the absorption spectra depending on the pH values of the surrounding water due to arrangement changes of TPPS adsorbed on TiO_2 film. The same behavior of the changes of absorption spectra but at different pH values as we reported previously[39] was observed. The absorption maxima of these spectra are listed in Table 1. Absorption bands observed at 414 nm in pH 6.5, and 428 and 482 nm in pH 1.6 for TPPS adsorbed on TiO_2 film were assigned to B-bands of the TPPS monomer, diprotonated TPPS monomer, and J-aggregates, respectively, according to the reported data.[7–19] The absorption spectra of TPPS on TiO_2 film in pH 1.6 water indicated that the diprotonated TPPS monomer and its J-aggregates coexisted on TiO_2 film, while only the TPPS monomer was adsorbed in pH 6.5 water.

Figure 2b shows the absorption spectra of the TPPS monomer in pH 9.8 (solid line), diprotonated TPPS monomer in pH 1.6 (broken line), and J-aggregates in pH 0.6 (dotted line) in aqueous solutions (5.65×10^{-6} M). The absorption peaks of these species in aqueous solutions were observed at 412, 433, and 490 nm in the absorption spectra of TPPS aqueous solu-

Table 1. Wavelength Showing the Maxima of pH-Dependent Absorption and Fluorescence Observed for TPPS on TiO_2 Film and TPPS in Aqueous Solutions

	pH	B-band/nm	Q-band/nm	Fluorescence/nm
on TiO_2	6.5	414	520, 555, 580, 655	660, 720
on TiO_2	1.6 (HCl)	428, 482	672, 695	—
in solution	9.8	412	515, 551, 579, 633	642, 702
in solution	1.6 (HCl)	433	593, 644	671, 724
in solution	0.6 (HCl)	433, 490	668, 705	671, 724

tions with different pH values, respectively (Table 1). The peak at 412 nm assigned to the TPPS monomer was observed only for a pH 9.8 solution. The peak at 433 nm assigned to the diprotonated TPPS monomer was observed only for a pH 1.6 solution. A pH 0.6 solution showed both the peaks at 433 and 490 nm, indicating the copresence of the diprotonated TPPS monomer and J-aggregates. The narrowed absorption band observed for J-aggregates is due to the coherent delocalization of excitons over an aggregate caused by the intermolecular interaction between transition dipole moments of TPPS molecules.[40] Between 500 and 700 nm, Q-bands of TPPS in an aqueous solution of pH 9.8 were observed at 515, 551, 579, and 633 nm attributed to [$Q_y(1,0)$, $Q_y(0,0)$, $Q_x(1,0)$, and $Q_x(0,0)$], respectively (the inset of Fig. 2b), while those at 593 and 644 nm attributed to [Q(1,0) and Q(0,0)], respectively, were observed in an aqueous solution of pH 1.6.

Corresponding to those absorption bands obtained with a pH 9.8 aqueous solution, four Q-bands at arround 520, 555, 580, and 655 nm were observed for TPPS on TiO_2 film in pH 6.5 water (the inset of Fig. 2a). Wavy spectra above 680 nm were due to interference attributed to multiple reflections of nanocrystalline TiO_2 film. In acidic water with pH 1.6, Q-bands of TPPS on TiO_2 film were observed at 672 and 695 nm. Absorbance of TPPS gradually decreased after replacing waters having different pH values. Decreases in the absorbances of Q-bands at 672 and 695 nm shown in Fig. 2a were not synchronous, meaning that the absorption bands at 672 and 695 nm should be derived from different species with each other. In the absorption spectra of an aqueous solution, the diprotonated TPPS monomer and its J-aggregates showed strong absorption bands at 644 and 705 nm in Q-bands region. Considering that the diprotonated TPPS monomer and its J-aggregates coexist on TiO_2 film in pH 1.6 water, the absorption bands at 672 and 695 nm should be assigned to the diprotonated TPPS monomer and its J-aggregates, respectively.

Figure 3 shows the fluorescence spectra of samples corresponding to those employed in Fig. 2. Figure 3a exhibits the fluorescence spectra of the TPPS monomer and diprotonated TPPS monomer on TiO_2 film in pH 6.5 and 1.6 waters measured with excitation wavelengths at 414 and 428 nm, respectively. In pH 6.5 water, the fluorescence bands assigned to $Q_x(0,0)$ and $Q_x(0,1)$ corresponding to absorption bands assigned to $Q_x(0,0)$ and $Q_x(1,0)$ were observed at 660 and 720 nm, respectively. On the other hand, fluorescence bands assigned to Q(0,0) and Q(0,1) in pH 1.6 water were not observed from TPPS on TiO_2 film. Repeated fluorescence measurements using waters having two different pH values (6.5 and 1.6) alternately showed alternating appearance and disappearance of the fluorescence spectra due to $Q_x(0,0)$ and $Q_x(0,1)$. The inset of Fig. 3a shows the changes of the fluorescence intensities at 660 nm. It was clearly displayed that drastic changes of the fluorescence intensities were induced reversibly depending on the pH values of the surrounding water. While a decrease in the fluorescence intensity was observed for the second measurement, the fluorescence intensity stayed constant after it. The fluorescence spectrum was also measured with excitation at the peak wavelength of J-aggregates on TiO_2 film (482 nm), but no fluorescence derived from J-aggregates was detected.

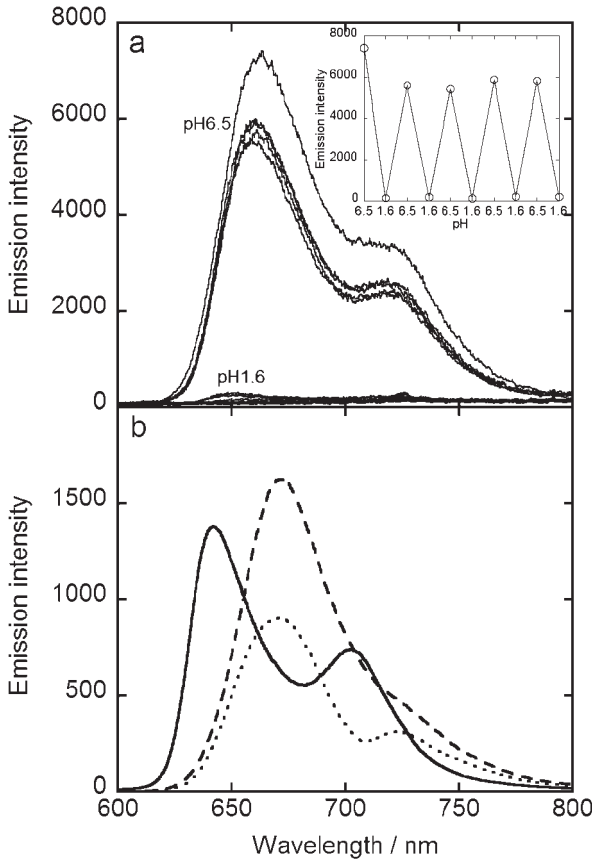

Fig. 3. Fluorescence spectra of TPPS on TiO_2 film and TPPS in solutions (5.65×10^{-6} M). Figure 3a shows reversible changes of fluorescence spectra of TPPS adsorbed on mesoporous TiO_2 film measured with excitation wavelength at 414 nm in pH 6.5 water and 428 nm in pH 1.6 water. The inset in Fig. 3a indicates the variations of fluorescence intensities at 660 nm (open circles). Fluorescence spectra of TPPS solutions having different pH values are shown in Fig. 3b; solid line: pH 9.8 solution, broken line: pH 1.6 solution, and dotted line: pH 0.6 solution.

Fluorescence spectra of the TPPS monomer (solid line, pH 9.8) and diprotonated TPPS monomer (broken line, pH 1.6; dotted line, pH 0.6) in aqueous solutions are shown in Fig. 3b. A TPPS aqueous solution of pH 0.6 (5.65×10^{-6} M) contained both the diprotonated monomer and J-aggregates as shown in Fig. 2b, as well as in the TPPS–TiO_2 system in pH 1.6 water. When a pH 1.6 solution containing only the diprotonated TPPS monomer was excited at 433 nm corresponding to the absorption of the diprotonated TPPS monomer, the fluorescence intensity was comparable with that of a pH 0.6 solution containing both the diprotonated monomer and J-aggregates. This is in clear contrast to how the TPPS–TiO_2 system containing both species showed no fluorescence in pH 1.6 water. When a pH 0.6 aqueous solution was excited at 490 nm corresponding to TPPS J-aggregates, only a weak fluorescence band at 717 nm corresponding to the Q-band of J-aggregates (707 nm) was obtained with a small Stokes shift of 197 cm^{-1} (no data in Fig. 3b), suggesting a non-radiative relaxation process of the excitation energy in J-aggregates.

Fluorescence Quenching of TPPS on TiO_2 Film in Acidic Water. The fluorescence of the diprotonated TPPS monomer on TiO_2 film was quenched drastically in pH 1.6, while such quenching was not observed in aqueous solutions. The ratios of diprotonated TPPS monomer on J-aggregates estimated using the absorption spectra were ≈25% in pH 0.6 aqueous solution and ≈70% on TiO_2 film in pH 1.6 water, respectively, and the remaining parts consisted of J-aggregates.

In our previous paper, it was reported that TPPS molecules form islands on TiO_2 film in spite of low coverage (5.1×10^{-2} molecule per nm^2).[39] The diprotonated TPPS monomer and its J-aggregates coexist in islands on TiO_2 film therein. Therefore, diprotonated TPPS monomers should be located in proximity to J-aggregates in islands on the TiO_2 surface. It has been reported that J-aggregates induce excitation energy transfer from the diprotonated monomer to J-aggregates depending on the distance between the J-aggregate and monomer.[41] Therefore, quenching of the fluorescence of the diprotonated TPPS monomer in pH 1.6 water should be attributed to energy transfer induced by the J-aggregate located closest to the diprotonated TPPS monomer. The energy transferred to J-aggregates should be dissipated as proven by the fact that no fluorescence was observed by the excitation of J-aggregates on TiO_2 film.

Excited molecules chemisorbed on TiO_2 film are generally quenched by efficient electron injection from the molecules into the conduction band of TiO_2.[27–34] It is known that protonation of TiO_2 film causes a positive shift (60 meV per a change of one pH value) of the conduction band edge of TiO_2 (−0.7 V vs SCE at pH 7.2).[25,42–47] This can facilitate electron injection from adsorbed molecules into TiO_2. Actually, it has been reported that electron-injection efficiency from a sensitizing dye into TiO_2 increases by protonation on the TiO_2 surface.[48] On the other hand, the oxidation potential of excited TPPS is −0.82 V vs SCE.[49] It has been theoretically estimated that the LUMO of diprotonated TPP (tetraphenylporphyrin) is ≈0.48 eV lower than that of TPP,[50] and then the shift of the oxidation potential could occur to TPPS by 0.48 eV, resulting in the lowering of the LUMO (−0.34 V) below the conduction band of TiO_2 (−0.36 V) at pH 1.6. We propose that fluorescence quenching of TPPS on TiO_2 is not mainly due to electron injection. However, there is no experimental evidence to deny the contribution of electron injection. Furthermore, the LUMO and conduction level are close to each other, which might lead to an electron transfer from diprotonated TPPS into TiO_2 in spite of a thermodynamically unfavorable condition. Consequently, contribution of the electron injection for the fluorescence quenching can not be excluded completely.

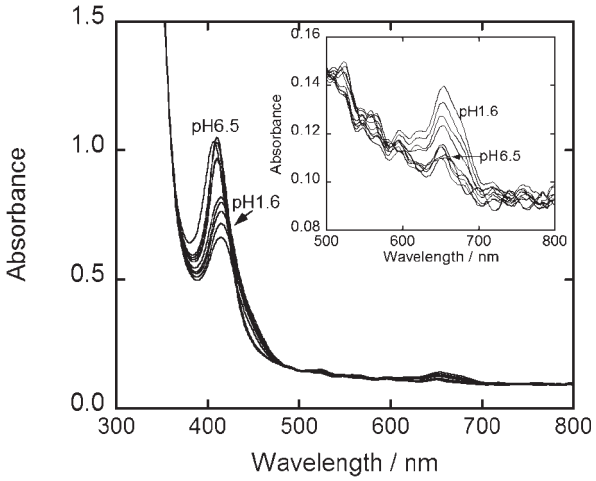

Fig. 4. Absorption spectra of TCPP on TiO_2 film in pH 6.5 and 1.6 waters. The inset indicates an enlarged illustration of Q-bands. pH Value of acidic water was controlled with HNO_3.

pH-Dependent Absorption Spectra of TCPP on TiO_2 Film. To investigate the effects of different anchoring groups bonded to porphyrin on the fluorescence behavior, TCPP was also examined. Figure 4 shows the absorption spectra of TCPP on TiO_2 film. It has been reported that TCPP molecules form J-aggregates in an aqueous solution acidified with HNO_3 and not with HCl.[51] Therefore, in a TCPP–TiO_2 system, HNO_3 was employed for the acidification of the surrounding water. TCPP–TiO_2 having a comparable absorbance to TPPS–TiO_2 was prepared by controlling the submersion time for dye-adsorption because the carboxyl group interacts strongly compared to the sulfonic acid group, causing an increase in the amount of adsorbed molecules. The B-band at 410 nm and four Q-bands at 524, 561, 597, and 652 nm were observed for TCPP on TiO_2 film in pH 6.5 water. By changing the pH value of the surrounding water from 6.5 to 1.6, the B-band shifted to 415 nm. Absorption maxima are listed in Table 2. In pH 1.6 water, absorbance at 652 nm, which was one of four Q-bands, increased compared to that in pH 6.5 water, while those of the other three Q-bands observed in pH 1.6 water were similar to those in pH 6.5 water. Absorption spectra of TCPP on TiO_2 film changed reversibly by alternate changes of pH values of the surrounding water between 6.5 and 1.6. TCPP J-aggregates in acidic aqueous water show a B-band at 467 nm.[19,51,52] The absence of the band around 467 nm attributed to J-aggregates in Fig. 4 indicated that no J-aggregates of TCPP on TiO_2 film were formed in pH 1.6 water acidified with HNO_3.

Two protons should be added to TCPP in pH 1.6 water.[8] Generally, diprotonated porphyrin shows two Q-bands like an absorpiton spectrum of metal porphyrin, while free-base porphyrin shows four Q-bands.[50] However, in the present

Table 2. Wavelength Showing the Maxima of pH-Dependent Absorption and Fluorescence Observed for TCPP on TiO_2 Film and TCPP in Aqueous Solutions

	pH	B-band/nm	Q-band/nm	Fluorescence/nm
on TiO_2	6.5	410	524, 561, 597, 652	660, 723
on TiO_2	1.6 (HNO_3)	415	530, 570, 597, 652	660, 723
in solution	9.8	414	517, 555, 581, 635	645, 704
in solution	1.6 (HCl)	402, 434	523, 559, 596, 652	670
in solution	0.6 (HCl)	417	622, 663	—
in solution	1.6 (HNO_3)	402, 434	522, 558, 596, 650	670
in solution	0.6 (HNO_3)	473, 509	669, 712	—

study, four Q-bands were still observed for TCPP on TiO_2 film even in pH 1.6 water. McHale et al. observed a similar spectrum of TCPP in an acidic aqueous solution showing four Q-bands[51,52] and concluded by measurements of resonance Raman spectra that TCPP molecules form dimers in an aqueous solution having a pH value of 1.2. The observation of four Q-bands was explained by symmetry-lowering perturbation in the dimer formation. Therefore, dimers of diprotonated TCPP should be formed on TiO_2 film in pH 1.6 water. Reversible changes of the absorption spectra shown in Fig. 4 indicate alternate changes between the TCPP monomer and dimer of diprotonated TCPP on TiO_2 film.

Figure 5 shows absorption spectra of TCPP in aqueous solutions having different pH values. The concentrations of all the TCPP aqueous solutions were 5.65×10^{-6} M, the same as that of the TPPS aqueous solutions employed in Figs. 2b and 3b. The wavelengths of the absorption maxima are listed in Table 2. All the Q-bands of TCPP on TiO_2 film in pH 6.5 water were shifted to longer wavelengths and only the B-band was blue-shifted, when compared to the absorption maxima of the TCPP monomer in a pH 9.8 aqueous solution.

Figure 5b shows absorption spectra of TCPP aqueous solutions having pH values of 1.6 and 0.6 acidified with HCl. The B-band of TCPP in a pH 1.6 aqueous solution was shifted to a longer wavelength (434 nm) (solid line in Fig. 5b) compared to that in a pH 9.8 solution (414 nm). As describe above, TCPP molecules form dimers of diprotonated TCPP in a pH 1.6 aqueous solution.[51,52] In a pH 0.6 TCPP aqueous solution, the B-band appeared at 417 nm. In addition, two Q-bands showed larger absorbance than those in a pH 1.6 aqueous solution (broken line in Fig. 5b), meaning formation of H-aggregates of TCPP in a pH 1.6 aqueous solution containing HCl.[51]

Figure 5c shows absorption spectra of TCPP aqueous solutions acidified with HNO_3. The absorption spectrum of a TCPP solution in pH 1.6 with HNO_3 (solid line in Fig. 5c) was similar to that with HCl (solid line in Fig. 5b), indicating formation of dimers of diprotonated TCPP, as describe above. In a pH 0.6 solution, absorption maxima were observed at 473 and 509 nm as B-bands and 669 and 712 nm as Q-bands (broken line in Fig. 5c). Both B- (473 and 509 nm) and Q-bands (669 and 712 nm) significantly shifted to longer wavelengths compared to those in a pH 9.8 solution (B-band: 414 nm, Q-bands: 517, 555, 581, and 635 nm), suggesting formation of TCPP J-aggregates, according to the theory of exciton splitting.[53]

Fluorescence Spectra of TCPP on TiO_2 Film. Figure 6 exhibits fluorescence spectra of TCPP on TiO_2 film (a) and in aqueous solutions (b). Fluorescence spectra of TCPP on TiO_2 film were measured with the excitation wavelength at

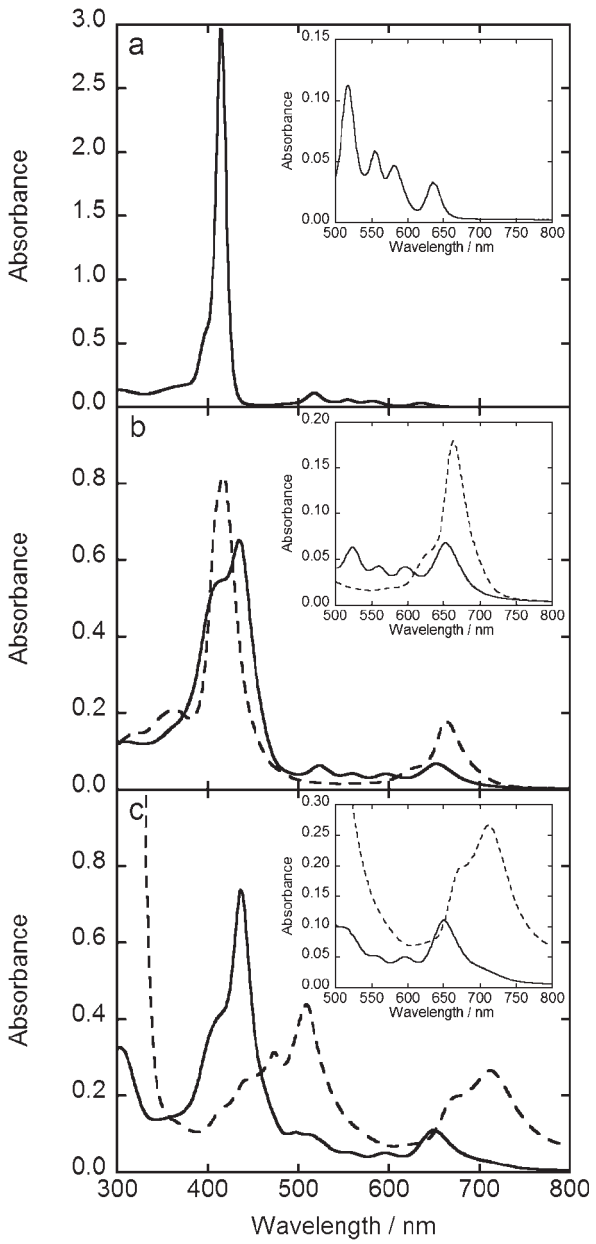

Fig. 5. Absorption spectra of TCPP in aqueous solutions (5.65×10^{-6} M) having different pH values; (a) pH 9.8 solution, (b) pH 1.6 solution (solid line) and pH 0.6 solution (broken line) acidified with HClaq, and (c) pH 1.6 solution (solid line) and pH 0.6 solution (broken line) acidified with HNO_3. The insets of Fig. 5 indicate enlarged illustrations of Q-bands.

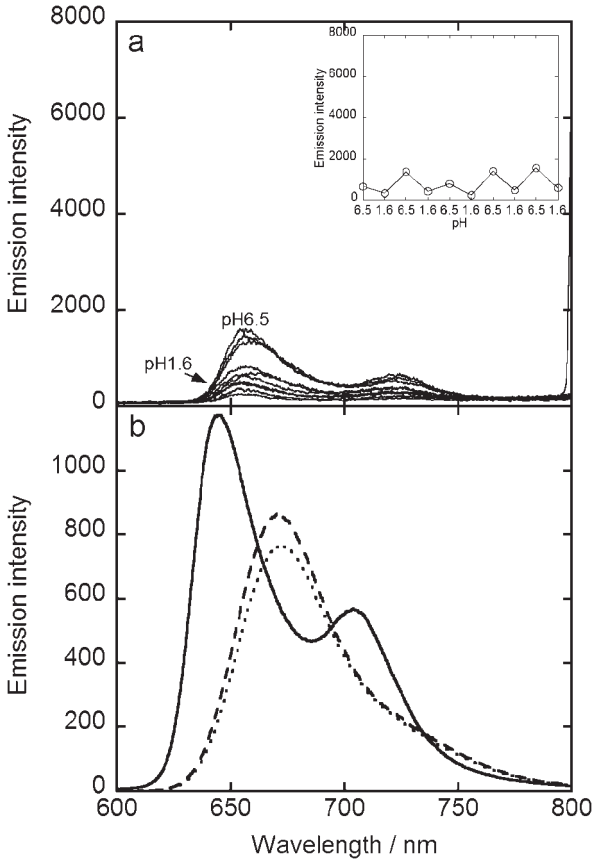

Fig. 6. Fluorescence spectra of TCPP on TiO_2 film in pH 6.5 water and pH 1.6 water with HNO_3 and TCPP in aqueous solutions (5.65×10^{-6} M). Figure 6a shows reversible changes of fluorescence spectra of TCPP adsorbed on mesoporous TiO_2 film measured with excitation wavelength at 410 nm in pH 6.5 water and 415 nm in pH 1.6 water. The inset in Fig. 6a indicates the variations of fluorescence intensities at 658 nm (open circles). Fluorescence spectra of TCPP solutions having different pH values are shown in Fig. 6b; solid line: pH 9.8 solution, broken line: pH 1.6 solution acidified with HCl, and dotted line: pH 1.6 solution acidified with HNO_3.

410 nm in a pH 6.5 water corresponding to a B-band of TCPP monomer, and 415 nm in pH 1.6 water acidified with HNO_3 corresponding to a B-band of a dimer of diprotonated TCPP. The fluorescence of the TCPP monomer on TiO_2 at 660 [$Q_x(0,0)$] and 723 nm [$Q_x(0,1)$] corresponding to absorption bands at 597 [$Q_x(1,0)$] and 652 nm [$Q_x(0,0)$] were observed in pH 6.5 water (Fig. 6a). On the other hand, the fluorescence was reduced by about 1/3 in pH 1.6 water acidified with HNO_3. Fluorescence spectra changed reversibly between the two cases by replacing water with pH 6.5 and pH 1.6 alternately (the inset in Fig. 6a). Fluorescence intensities of TCPP on TiO_2 film in pH 6.5 water were much weaker than those of TPPS on TiO_2 film at the same conditions. Supposing that the oxidation potential of excited TCPP is close to that of TPPS,[49] the weak fluorescence of TCPP on TiO_2 film in pH 6.5 water might be due to quenching caused by efficient electron injection from the excited state of porphyrin through the carboxyl group to TiO_2 film. The fluorescence of TCPP adsorbed on TiO_2 film was not completely quenched in pH 1.6 water in contrast to TPPS adsorbed on TiO_2. Quenching of the fluorescence of TCPP adsorbed on TiO_2 film in pH 1.6 water would be due to the electron-injection process and energy-dissipation process occurring to dimers of diprotonated TCPP aggregated on the surface of TiO_2.

Fluorescence spectra of TCPP in aqueous solutions (5.65×10^{-6} M) having different pH values are shown in Fig. 6b. Excitation wavelengths were set at 414 nm in pH 9.8 water and 434 nm in pH 1.6 water acidified with HCl and HNO_3, respectively, for recording fluorescence spectra of a TCPP monomer solution (solid line) and diprotonated TCPP dimer solutions with HCl (broken line) and HNO_3 (dotted line). The same fluorescence spectra of the dimer of diprotonated TCPP were obtained from the two types of pH 1.6 aqueous solutions using HCl and HNO_3. Those three solutions gave fluorescence spectra with the same level of fluorescence intensities; that is, the fluorescence intensity of the dimer of diprotonated TCPP in pH 1.6 was close to that of the TCPP monomer in a pH 9.8 solution. Therefore, only fluorescence quenching of dimers of diprotonated TCPP aggregated densely on TiO_2 film would cause the dissipation of excitation energy occurring to TCPP adsorbed on TiO_2 film in pH 1.6 water. The weaker fluorescence intensities of TPPS on TiO_2 film in low-pH water than those of TCPP on TiO_2 film could be explained by the different deactivation processes: deactivation of the excited diprotonated TPPS monomer by J-aggregates, while deactivation of the excited dimer of diprotonated TCPP by neighboring dimers.

pH-Dependent Quenching Mechanisms of TPPS–TiO_2 and TCPP–TiO_2 Systems. In this study, it has been found that the fluorescence intensity of water-soluble porphyrin on TiO_2 film depends on the pH value of the surrounding water. A schematic diagram of the pH-dependent quenching mechanism of porphyrins on TiO_2 is shown in Fig. 7. TPPS on TiO_2 film emits strongly in pH 6.5 water (a), while it does not emit in pH 1.6 water (b). On the other hand, TCPP on TiO_2 film shows weak fluorescence intensity in pH 6.5 water (c) and fluorescence is quenched in pH 1.6 water (d). Furthermore, these changes in the fluorescence are reversibly repeated by the changing pH value of the surrounding water. It has been proposed that the main factor determining fluorescence intensity in pH 6.5 water is the electron-injection efficiency from excited porphyrin into the conduction band of TiO_2. LUMO levels of TPPS and TCPP locate energetically higher than the conduction edge of TiO_2, enabling the porphyrin–TiO_2 system to undergo a charge separation. Electron-injection efficiency depends on the interaction between the TiO_2 surface and the anchoring group of the adsorbent. Since the carboxyl group can interact strongly compared to the sulfonic acid group, the fluorescence of TCPP is more efficiently quenched on TiO_2 film in pH 6.5 water. On the other hand, another process causing fluorescence quenching in pH 1.6 water has been suggested: J-aggregates-induced deactivation. Deactivation of the excited diprotonated TPPS monomer occurs by efficient energy transfer from the diprotonated TPPS monomer to surrounding J-aggregates, resulting in a drastic fluorescence quenching. Deactivation of the excited dimer of diprotonated TCPP is also induced by the interaction with surrounding dimers of diprotonated TCPP in pH 1.6 water. The fluorescence of the porphy-

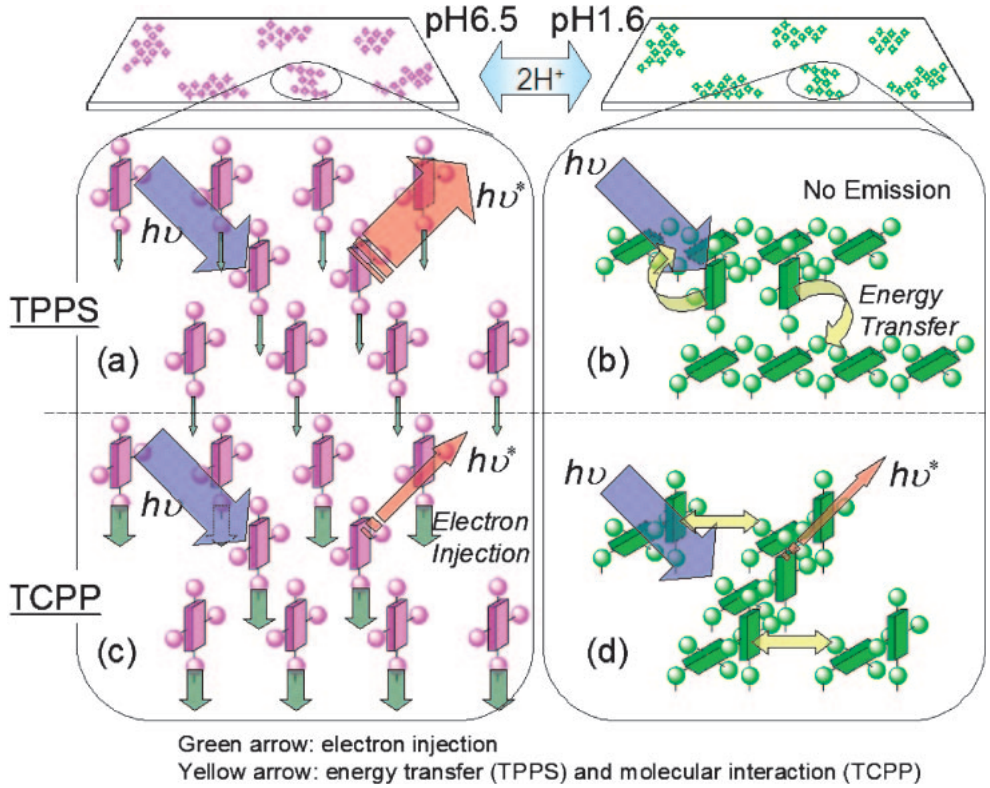

Fig. 7. A schematic diagram of pH-dependent quenching mechanism of TPPS and TCPP on TiO_2 surface. Porphyrin molecules form molecular islands on TiO_2 surface. (a and c) In pH 6.5 water, both water-soluble porphyrin molecules are present as a monomer on TiO_2 film. Quenching of excited porphyrin molecules is due to the electron injection from porphyrin into TiO_2. In pH 1.6 water, (b) TPPS forms J-aggregates while (d) TCPP forms dimers. Deactivation of excitation energy is induced by aggregated species.

rin derivatives can be switched depending on the molecular states, bimolecular arrangement, molecular assembly, and energetics of the systems, which are controlled by molecular structures and the pH value of the surrounding environment.

Conclusion

pH-Dependent fluorescence spectral changes of water-soluble porphyrin derivatives have been investigated. TPPS on TiO_2 film shows fluorescence switching by changing the pH values of the surrounding water. On the other hand, the fluorescence intensities of TCPP on TiO_2 film changes less by varying pH values than those of TPPS on TiO_2 film. The fluorescence intensities of water-soluble porphyrin derivatives depend on the efficiency of electron injection through the anchoring group and are influenced by the aggregates-induced deactivation of emitting species. This study has demonstrated that selecting an appropriate anchoring group of adsorbent and controlling the molecular arrangement on TiO_2 film leads to a fluorescence switching system driven by the pH change of the surrounding environment.

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