pH-Dependent reversible transformation of $TPPS_4$ anchored on mesoporous TiO_2 film between monomers and J-aggregates

Yusuke Fujii,[a] Yasuchika Hasegawa,[a] Shozo Yanagida[b] and Yuji Wada*[a]

Received (in Cambridge, UK) 2nd March 2005, Accepted 18th April 2005
First published as an Advance Article on the web 10th May 2005
DOI: 10.1039/b502991k

Protonated $TPPS_4$ monomer and its J-aggregate were formed simultaneously from $TPPS_4$ adsorbed through its sulfonic acid groups on TiO_2 porous film by decreasing the pH of the surrounding water and this behavior on TiO_2 film can be reversibly repeated depending on pH, indicating a flexible and stable arrangement of $TPPS_4$ through chemical bonds between the sulfonic acid groups and the TiO_2 surface.

J-Aggregates, which were discovered by Jelley and Scheibe,[1] show quite narrow absorption bands attributed to intermolecular interactions between transition dipole moments causing a delocalization of excitons over the aggregate.[2] 5,10,15,20-Tetraphenylporphine tetrasulfonic acid, which is often abbreviated as $TPPS_4$, is a well-known water soluble metal-free porphyrin which can form J-aggregates in acidic water or in the presence of various organic and inorganic cations.[3] $TPPS_4$ in a solution has been studied extensively to reveal some specific characteristics of J-aggregates because the $TPPS_4$ J-aggregate can be regarded as a model aggregate derived from the high symmetry of the porphyrin ring and some interesting photophysical properties have been elucidated.[4]

Molecular arrangements on solid substrates play an important role in vital functions such as photosynthesis and preparation of artificially ordered molecular structures is attractive from the life-scientific or optoengineering points of view. Static states of $TPPS_4$ J-aggregate films on solid surfaces have been studied.[5] On the other hand, Takagi *et al.* reported that the alignment of non-aggregated cationic porphyrin molecules on clay surfaces can be controlled dynamically by changing the surrounding solvent.[6] But pH-depending dynamic aggregation of $TPPS_4$ on solid substrate has not been studied so far.

To study pH-dependent spectral change of $TPPS_4$ on solid substrates, $TPPS_4$ molecules need to be stabilized on solid surfaces because $TPPS_4$ is easily dissolved in water. In this work, mesoporous TiO_2 thin films have been introduced as a substrate to anchor $TPPS_4$ because molecules having an anchoring group such as –COOH, $–PO_3H_2$ or $–SO_3H$ can be adsorbed on TiO_2 surfaces *via* chemical bonds,[7] which results in a strong interaction compared to physical adsorption by van der Waals forces. Furthermore, mesoporous TiO_2 thin film has a quite large surface area that enables one to measure the absorption spectrum of the molecules adsorbed even as a monolayer on the surface with a sufficient optical density. Thus we have studied the change in the absorption spectra of $TPPS_4$ monolayers anchored on mesoporous TiO_2 films dipped in water of controlled pH and found that the behavior of $TPPS_4$ as an assembly depends on the pH value, which has not previously been observed in solution.

5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine-*p*,*p′*,*p″*,*p‴*-tetrasulfonic acid tetrasodium salt hydrate ($H_2TPPS_4^{4-}$) was purchased from Aldrich and used without further purification. In this communication, $H_4TPPS_4^{2-}$ is defined as an acidic type of $TPPS_4$ having an extra $2H^+$ at the center of the porphyrin ring in an acidic medium ($pK_a = 4.8$).[8] A mesoporous TiO_2 thin film with a thickness of 2.6 μm was prepared with a colloidal TiO_2 paste purchased from Solaronix. The TiO_2 paste was spread onto a fluorine-doped SnO_2 glass substrate and dried in air. The film was sintered at 450 °C for 30 minutes and a transparent TiO_2 film, which was suitable for measurements of absorption spectra in transmittance mode, was obtained. $H_2TPPS_4^{4-}$ was dissolved in DMF (solution 1, 3×10^{-4} mol l^{-1}) or DMF containing HClaq (solution 2, 3×10^{-4} mol l^{-1}) and the films were dipped into the two kinds of the solutions overnight. The $TPPS_4$-adsorbing TiO_2 film was washed with ethanol thoroughly and dried in air. Absorption spectra of the dry TiO_2 films were measured without surrounding water. Then the TiO_2 film immersed in solution 1 was placed into a 1 cm × 1 cm optical cell containing deionized water. The pH of the water in the quartz cell was adjusted by adding HClaq. A series of measurements were made, using water at different pH each time. Solution 2, which was prepared by adding HClaq to $TPPS_4$–DMF solution, was used with the intention of making $TPPS_4$ J-aggregates on TiO_2.

Fig. 1 shows the absorption spectra of the above two mesoporous TiO_2 films dipped into the $TPPS_4$ solutions 1 and

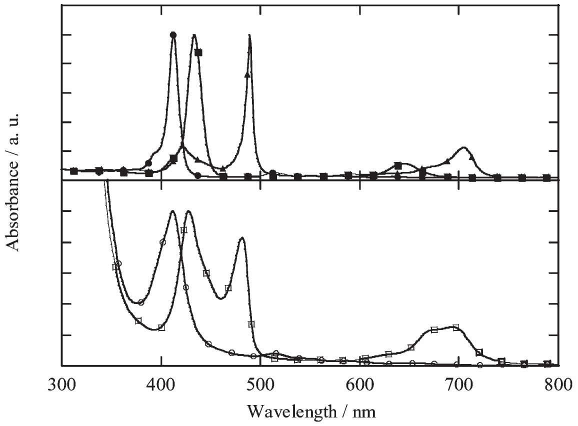


Fig. 1 Absorption spectra of $TPPS_4$ on TiO_2 without surrounding water (lower) and in water (upper); open circles: $H_2TPPS_4^{4-}$ on TiO_2, open squares: $H_4TPPS_4^{2-}$ on TiO_2, filled circles: $H_2TPPS_4^{4-}$ in water (pH 6.9), filled squares: $H_4TPPS_4^{2-}$ monomer in water (pH 2.2), filled triangles: $H_4TPPS_4^{2-}$ J-aggregate in water (pH 0.3).

---

*ywada@mls.eng.osaka-u.ac.jp

solution 2 respectively, and those of $TPPS_4$ in neutral water (pH 6.9) and water acidified with HClaq (pH 2.2 and pH 0.3). The concentration of $TPPS_4$–H_2O solution was 3.43×10^{-5} mol l^{-1}. The absorption maximum observed for $H_2TPPS_4^{4-}$ in neutral water at 413 nm was assigned to the B (Soret) band, confirming the same assignment of the absorption observed for $H_2TPPS_4^{4-}$ on mesoporous TiO_2 film at 414 nm shown in the lower spectrum of Fig. 1. The spectrum observed for the aqueous solution at pH 2.2 showed an absorption maximum at 434 nm assigned to the B band of $H_4TPPS_4^{2-}$ monomer (denoted as the MB band), while a narrow absorption band, which was attributed to the $H_4TPPS_4^{2-}$ J-aggregate, appeared at 489 nm (denoted as the JB band) in pH 0.3 water. The Q bands were also observed, but we referred only to the B bands since these could be distinguished more clearly than the Q bands. The absorption spectrum of $H_4TPPS_4^{2-}$ on mesoporous TiO_2 film which was dipped into solution 2 showed the two B bands at 428 and 482 nm. These absorption bands were assigned to the MB band and the JB band of $H_4TPPS_4^{2-}$ on TiO_2, respectively, although both absorption bands were shifted a little bit to shorter wavelength compared to the spectra of both solutions at pH 2.2 and pH 0.3. Consequently, all absorption spectra of $TPPS_4$ on TiO_2 were well assigned by comparing to those in water.

Fig. 2 shows the absorption spectra of $TPPS_4$ in water (3.43×10^{-5} mol l^{-1}) having various hydrogen ion concentrations from pH 6.9 to pH 0.3 measured using a 1 mm quartz cell. The inset shows changes of the absorbances at 413, 434 and 489 nm depending on the pH values in $TPPS_4$ aqueous solution. This indicated that when the pH of a $TPPS_4$ solution was decreased gradually, $H_4TPPS_4^{2-}$ J-aggregates were formed in two steps from $H_2TPPS_4^{4-}$ monomer *via* $H_4TPPS_4^{2-}$ monomer. Scheme 1 displays this two-step route from $TPPS_4$ in neutral medium to J-aggregates, already reported.[9]

Fig. 3 shows changes in the absorption spectra of $TPPS_4$ on mesoporous TiO_2 films, measured in water of various concentrations of hydrogen ion, from pH 6.5 to pH 1.2. It should be mentioned that a colored TiO_2 film with $TPPS_4$ showed extreme bleaching under the high concentration of hydrogen ions, pH < 1.

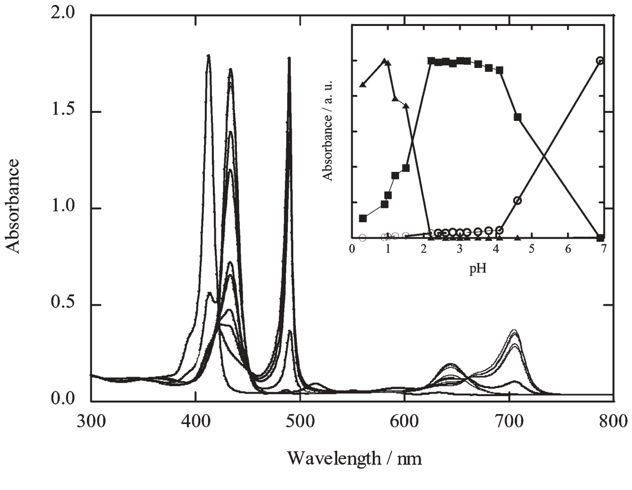
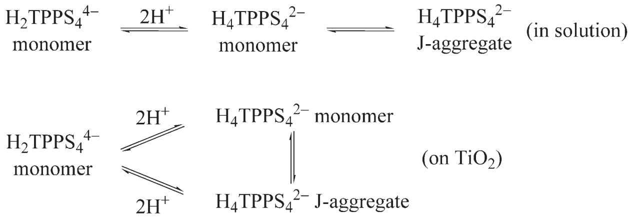


Fig. 2 Absorption spectra of $TPPS_4$ in water (3.43×10^{-5} mol l^{-1}) having various pH values. The inset shows absorbance changes at 413 (open circles), 434 (filled squares) and 489 nm (filled triangles) depending on pH values.



Scheme 1 Equilibrium relationship of $TPPS_4$ on TiO_2 and in water.

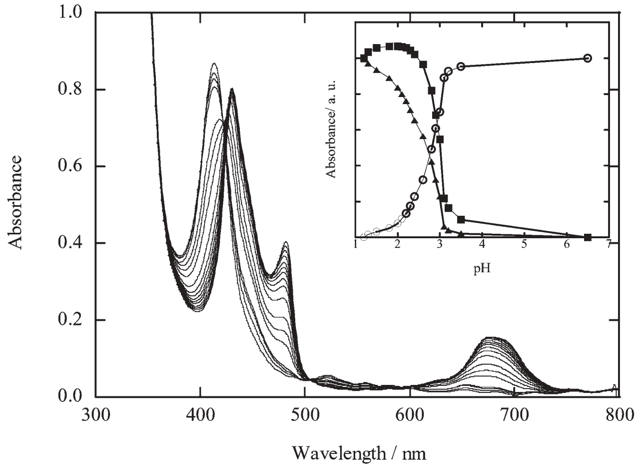


Fig. 3 Absorption spectra of $TPPS_4$ on TiO_2 in water depending on pH. The inset shows changes in absorbance at 414 (open circles), 428 (filled squares) and 482 nm (filled triangles) at pH 6.5 to pH 1.2. $TPPS_4$-adsorbed TiO_2 film was prepared using solution 1.

Under neutral conditions, only one B band derived from $H_2TPPS_4^{4-}$ at 414 nm was observed. When the pH was changed by changing the concentration of HClaq, the absorbance at 414 nm was decreased. Especially it diminished drastically in the range from pH 3 to pH 2, accompanied by an increase in the absorbance of $H_4TPPS_4^{2-}$ at 428 and 482 nm shifting to longer wavelength compared to the absorption bands of $H_2TPPS_4^{4-}$. An increase in the JB band at 482 nm indicated the formation of its J-aggregate as demonstrated in Fig. 1. The isosbestic points observed in Fig. 3 indicated a stoichiometric conversion between $H_2TPPS_4^{4-}$ monomer and $H_4TPPS_4^{2-}$ monomer, and between $H_2TPPS_4^{4-}$ and $H_4TPPS_4^{2-}$ J-aggregate on TiO_2, shown in Scheme 1. This behavior of the spectral change depending on the pH values occurring on mesoporous TiO_2 film was absolutely different from that in an aqueous $TPPS_4$ solution. Therefore the behavior depending on the pH value shown in Fig. 3 was regarded as a specific spectroscopic phenomenon only observed for $TPPS_4$ anchored on TiO_2 surface. The inset of Fig. 3 shows the changes in the absorbances at 414, 428 and 482 nm along with the changes in the pH values. The absorption at 428 nm assigned to $H_4TPPS_4^{2-}$ monomer increased gradually with increasing concentration of hydrogen ion, but reached a constant at pH 2.5 and decreased below pH 1.5, while the absorbance at 482 nm attributed to J-aggregates went on increasing. This behavior suggested a partial route for the formation of J-aggregates from the $H_4TPPS_4^{2-}$ monomer in addition to a direct route from $H_2TPPS_4^{4-}$ occurring in parallel with the formation of $H_4TPPS_4^{2-}$.

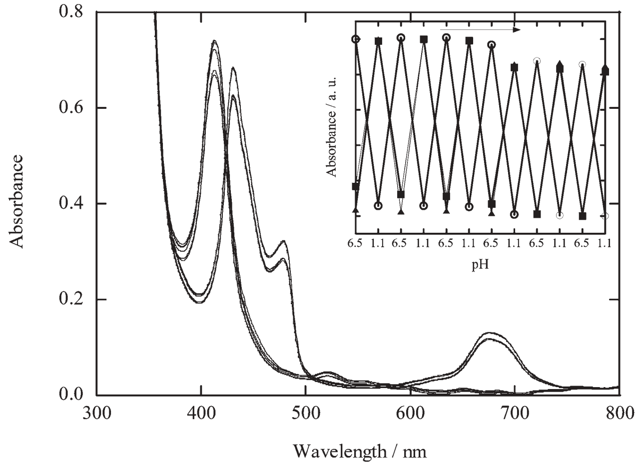


Fig. 4 Reversible changes of absorption spectra of $TPPS_4$ immobilized on mesoporous TiO_2 film. The inset indicates an absorbance at 414 (open circles), 428 (filled squares) and 482 nm (filled triangles) in pH 6.5 and pH 1.1. $TPPS_4$-adsorbed TiO_2 film was prepared using solution 1.

Fig. 4 shows the change in the absorption spectra of $TPPS_4$ on mesoporous TiO_2 films measured on changing the pH value between pH 6.5 and pH 1.1, alternately. The inset showing the repeated appearance and disappearance of the $H_4TPPS_4{}^{2-}$ monomer and J-aggregate by changing the pH values indicated that almost the same spectral shapes were reproduced repeatedly at each pH value, although the absorption spectra of $TPPS_4$-adsorbed TiO_2 lost optical density to some extent because of the strong acid, pH = 1.1, causing a desorption of $TPPS_4$ from TiO_2. When mesoporous TiO_2 film was dipped into a $H_2TPPS_4{}^{4-}$ solution, $H_2TPPS_4{}^{4-}$ was adsorbed disorderly as a monolayer on the mesoporous TiO_2 film. Therefore the reversibility of the absorption spectra shown in Fig. 3 indicated that $TPPS_4$ on TiO_2 film can be aligned between disordered and ordered arrangements depending on pH, although porphyrin molecules are fixed through chemical bonds on TiO_2. This behavior is not available to molecular films on solid surfaces based on physical adsorption such as LB films, but only for chemically anchored molecules on surfaces.

In the case of $TPPS_4$-adsorbed mesoporous TiO_2 film prepared using solution 1, the amount of $TPPS_4$ on TiO_2 film per effective area was 8.5×10^{-12} mol cm^{-2}, corresponding to only 5.1×10^{-2} molecules nm^{-2}. Therefore it can be strongly suggested that $TPPS_4$ molecules form islands when they are adsorbed on TiO_2 film, and form J-aggregates in acidic water. $TPPS_4$ molecules might form weak assemblies due to π–π interactions between porphyrin rings, reflected on the formation of islands in the adsorption. The spectral shapes of J-aggregates on TiO_2 films shown in Fig. 1, 3 and 4 were similar to the spectrum which indicated the existence of J-aggregates with a long slipping distance between porphyrin molecules.[10]

One of the authors (Y.F.) is grateful for the financial support of the center of excellence (21 COE) program "Creation of Integrated Ecochemistry" of Osaka University. This work was supported by a Grant-in-Aid for Scientific Research (No. 12450345) and a Grant-in-Aid for Scientific Research on Priority Areas (417) (No. 15033245) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

Yusuke Fujii,[a] **Yasuchika Hasegawa,**[a] **Shozo Yanagida**[b] **and Yuji Wada***[a]
[a] *Material and Life Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka Suita, 565-0871, Japan.*
E-mail: ywada@mls.eng.osaka-u.ac.jp
[b] *Center for Advanced Science and Innovation, Osaka University, Japan.*
E-mail: yanagida@mls.eng.osaka-u.ac.jp

Notes and references

1 E. E. Jelley, *Nature*, 1936, **138**, 1009; G. Scheibe, *Angew. Chem.*, 1936, **49**, 563.
2 M. Y. Choi, J. A. Pollard, M. A. Webb and J. L. McHale, *J. Am. Chem. Soc.*, 2003, **125**, 810; H. Kano, T. Saito and T. Kobayashi, *J. Phys. Chem. A*, 2001, **105**, 413; L. Kelbauskas, S. Bagdonas, W. Dietel and R. Rotomskis, *J. Lumin.*, 2003, **101**, 253.
3 E. B. Fleischer, J. M. Palmer, T. S. Srivastava and A. Chatterjee, *J. Am. Chem. Soc.*, 1971, **93**, 3162; R. F. Pasternack, P. R. Huber, P. Boyd, G. Engasser, L. Francesconi, E. Gibbs, P. Fasella, G. C. Venturo and L. deC. Hinds, *J. Am. Chem. Soc.*, 1972, **94**, 4511; N. C. Maiti, S. Mazumdar and N. Periasamy, *J. Phys. Chem. B*, 1998, **102**, 1528.
4 O. Ohno, Y. Kaizu and H. Kobayashi, *J. Chem. Phys.*, 1993, **99**, 4128; J. M. Ribó, J. Crusats, F. Sagués, J. Claret and R. Rubires, *Science*, 2001, **292**, 2063; H. Kano and T. Kobayashi, *J. Chem. Phys.*, 2002, **116**, 184.
5 L. Zhang, Q. Lu and M. Liu, *J. Phys. Chem. B*, 2003, **107**, 2565; L. Zhang, J. Yuan and M. Liu, *J. Phys. Chem. B*, 2003, **107**, 12768; C. Guo, B. Ren and D. L. Akins, *J. Phys. Chem. B*, 1998, **102**, 8751; W. Xu, H. Guo and D. L. Akins, *J. Phys. Chem. B*, 2001, **105**, 1543; A. S. R. Koti and N. Periasamy, *Chem. Mater.*, 2003, **15**, 369; R. Rotomskis, R. Augulis and V. Snitka, *J. Phys. Chem. B*, 2004, **108**, 2833.
6 S. Takagi, M. Eguchi and H. Inoue, *Res. Chem. Intermed.*, in press.
7 K. Kalyanasundaram and M. Grätzel, *Coord. Chem. Rev.*, 1998, **77**, 347; K. Kilså, E. I. Mayo, B. S. Brunschwig, H. B. Gray, N. S. Lewis and J. R. Winkler, *J. Phys. Chem. B*, 2004, **108**, 15640; T. Ma, K. Inoue, H. Noma, K. Yao and E. Abe, *J. Photochem. Photobiol. A*, 2002, **152**, 207; W. M. Campbell, A. K. Burrell, D. L. Officer and K. W. Jolley, *Coord. Chem. Rev.*, 2004, **248**, 1363; X. Yang, Z. Dai, A. Miura and N. Tamai, *Chem. Phys. Lett.*, 2001, **334**, 257.
8 E. Bellacchio, R. Lauceri, S. Gurrieri, L. M. Scolaro, A. Romeo and R. Purrello, *J. Am. Chem. Soc.*, 1998, **120**, 12353.
9 N. C. Maiti, M. Ravikanth, S. Mazumdar and N. Periasamy, *J. Phys.Chem.*, 1995, **99**, 17192; D. L. Akins, S. Özçelik, H.-R. Zhu and C. Guo, *J. Phys. Chem.*, 1996, **100**, 14390; M. A. Castriciano, A. Romeo, V. Villari, N. Micali and L. M. Scolaro, *J. Phys. Chem. B*, 2003, **107**, 8765; B. Ren, Z.-Q. Tian, C. Guo and D. L. Akins, *Chem. Phys. Lett.*, 2000, **328**, 17.
10 S. Okada and H. Segawa, *J. Am. Chem. Soc.*, 2003, **125**, 2792.