Suppressed Deactivation of Excited Porphyrin by Formation of Inclusion Complex with Cyclodextrin on Mesoporous TiO₂ Film

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HP-β-CD–porphyrin inclusion complexes were formed on TiO₂ film by use of water-soluble porphyrin such as TCPP and TPPS, respectively. Quite intense fluorescence spectra of porphyrins were recovered by formation of the inclusion complex due to suppression of excitation energy hopping occurring between porphyrin molecules on TiO₂.

Cyclodextrins (CDs) are cyclic oligosaccharides having a hydrophobic cavity in the molecular center made up of six, seven, and eight D-glucose (α-CD, β-CD, and γ-CD, respectively). The formation of inclusion complexes composed of porphyrin and CDs provides us much scientific interests because of the modification of various properties of porphyrin. CD–porphyrin inclusion complexes are representative supramolecular systems having mimicking functions of biological materials. Recently, Kano et al. reported a novel myoglobin model composed of CD–porphyrin inclusion complex.[1] The photophysical[2–8] and electrochemical properties[9] of CD–porphyrin in solution were investigated and formation constants of water-soluble porphyrin with some CDs were determined. However, unique properties of inclusion complexes on solid surface have not been reported so far.

Dye-sensitized solar cells are promising as low-cost solar cells and have been studied greatly since 1991.[10] Excitation energy deactivation of dye on TiO₂ is due to not only the electron injection from the excited sensitizer into conduction band of TiO₂,[11–14] but also the excitation energy hopping between dyes located close to each other.[14,15] In the present study, we have found that fluorescence intensity of water-soluble porphyrin such as tetrakis(4-carboxyphenyl)porphyrin (TCPP) and tetrakis(4-sulfonatophenyl)porphyrin (TPPS) chemisorbed on TiO₂ was increased drastically by the formation of 2:1 inclusion complex composed of hydroxypropyl-β-CD (HP-β-CD), showing the suppression of the excitation energy deactivation occurring on the surface.

Commercially available HP-β-CD, TCPP, and TPPS were used without further purification. TiO₂ paste was purchased from Solaronix. Transparent mesoporous TiO₂ film was prepared by spreading TiO₂ paste onto a glass substrate and then it was sintered at 450 °C for 30 min. TiO₂ films were immersed into a TCPP–DMF solution (3.0×10^{-4} M) (denoted as TCPP–TiO₂) or an aqueous solution containing 2:1 molar ratio of HP-β-CD (1.0×10^{-2} M) and TPPS (5.0×10^{-3} M) (denoted as HP-β-CD–TPPS–TiO₂), respectively. TCPP–TiO₂ systems were immersed into a cyclodextrin aqueous solution (1.0×10^{-3} M) for making HP-β-CD–TCPP on the surface of the film (denoted as HP-β-CD–TCPP–TiO₂) or into water without any additives for the control experiment for 30 min, respectively. After TiO₂ films adsorbing HP-β-CD–TCPP and HP-β-CD–TPPS were dried with vigorous gas flow, they were placed into 10 mm optical cells, respectively. Then absorption and fluorescence measurements of those films were carried out with Hitachi U3300 spectrophotometer and Hitachi F4500 spectrofluorometer at room temperature. ¹H NMR spectrum of 5.0×10^{-3} M TPPS in D₂O containing 1.0×10^{-2} M HP-β-CD was measured at 270 MHz.

Figure 1 shows absorption (a) and fluorescence spectra (b) of TCPP–TiO₂ (solid lines) and HP-β-CD–TCPP–TiO₂ (broken lines). In the absorption spectrum observed for TCPP–TiO₂ (Figure 1a), Soret band of TCPP was shifted to shorter wavelength and broadened compared to that in an aqueous solution (Supporting Information). Therefore, TCPP monomer and its H-aggregates could coexist on TiO₂ film. Soret band of HP-β-CD–TCPP–TiO₂ was observed at 417 nm, while 404 nm for TCPP–TiO₂. It is obvious that Soret band of TCPP on TiO₂ was shifted to longer wavelength by the inclusion into HP-β-CD. The same phenomenon has been reported in a solution system.[4–6] In Figure 1b, drastically strong fluorescence was observed for HP-β-CD–TCPP–TiO₂ compared to that of TCPP–TiO₂. Since it has been reported that cyclodextrin induces the dissociation of porphyrin aggregates in an aqueous solution,[16] porphyrin molecules chemisorbed on TiO₂ film would be separated with each other by the formation of the inclusion complexes. The separation of porphyrin molecules induced by the formation of the inclusion complex should suppress the energy hopping. Therefore, it is reasonable to consider that the suppression of energy hopping is a major reason for fluorescence recovery. However, we can not exclude a possibility of the suppression of electron injection for fluorescence recovery.[14,15] It was confirmed that no significant change of fluorescence intensity was observed in a solution system by adding HP-β-CD (Supporting Information).

In HP-β-CD–TCPP system, both 1:1 and 2:1 inclusion complexes could exist on TiO₂. Therefore, in order to clarify the contribution of each complex to the suppression of the excitation energy, the 2:1 inclusion complex of TPPS in aqueous
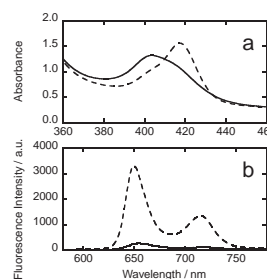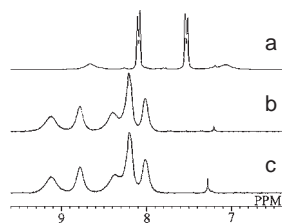

Figure 1. Absorption (a) and fluorescence spectra (b) of TCPP (solid lines) and HP-β-CD–TCPP (broken lines) chemisorbed on mesoporous TiO₂ films.
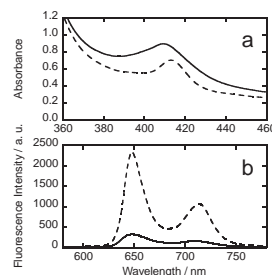
solution was prepared in advance and then adsorbed on TiO_2 film. TPPS was employed instead of TCPP in this experiment because of its high solubility in water.

The existence of the 2:1 complex can be confirmed by ^{1}H NMR spectra. Figure 2 shows NMR spectra of a D_2O solution of 5.0×10^{-3} M TPPS (a), a D_2O solution of 5.0×10^{-3} M TPPS containing 1.0×10^{-2} M HP-β-CD (b), and a D_2O solution of 5.0×10^{-3} M TPPS containing excess amount of HP-β-CD (10 times equivalent) (c). All signals attributed to protons in TPPS were assigned by 1D and 2D NMR analyses. By addition of HP-β-CD, all NMR signals derived from TPPS shifted to lower magnetic field, indicating the formation of inclusion complexes (Figures 2b and 2c). The NMR spectrum of a D_2O solution containing 2:1 molar ratio of HP-β-CD and TPPS (Figure 2b) was almost the same as that of a TPPS solution containing excess amount of HP-β-CD (Figure 2c). It has been reported that the 2:1 HP-β-CD–TPPS inclusion complex is formed in an aqueous solution under excess amount of HP-β-CD and the formation constant of TPPS with HP-β-CD is 10^7 order for 2:1 inclusion complex.[4,6] Therefore, it was concluded that only 2:1 inclusion complex was contained in an aqueous solution of 5.0×10^{-3} M TPPS containing 1.0×10^{-2} M HP-β-CD.

The 2:1 inclusion complex prepared in advance was adsorbed on TiO_2 film by immersing it into an aqueous solution of 5.0×10^{-3} M TPPS containing 1.0×10^{-2} M HP-β-CD. The state of 2:1 HP-β-CD–TSPP inclusion complex should be kept even after porphyrin-adsorption because steric repulsion between cyclodextrin of inclusion complex and TiO_2 surface should not affect the process of porphyrin-adsorption on TiO_2. Figure 3 displays absorption (a) and fluorescence spectra (b) of TPPS and the 2:1 inclusion complex on TiO_2 film. Absorption bands of TPPS and the 2:1 inclusion complex (HP-β-CD–TPPS) were observed at 409 and 413 nm, respectively. Figure 3a clearly shows the red shift of Soret band due to inclusion of TPPS into HP-β-CD. The absorbance observed for HP-β-CD–TPPS–TiO_2 was less than that observed for TPPS–TiO_2 due to the decrease of the amount of adsorbed TPPS caused by the formation of the bulky inclusion complex. In Figure 3b, it is obvious that the inclusion complex of TPPS into HP-β-CD gave the strong fluorescence even on TiO_2 film, demonstrating the similar phenomenon to that shown in Figure 1b. Drastic recovery of the fluorescence intensity by inclusion into HP-β-CD was commonly observed for porphyrin derivatives chemisorbed on TiO_2 film. Therefore, we have reached a conclusion that deactivation of excitation energy of porphyrin molecules chemisorbed on TiO_2 film is effecively suppressed by making inclusion complex into HP-

Figure 3. Absorption (a) and fluorescence spectra (b) of TPPS (solid lines) and HP-β-CD–TPPS (broken lines) chemisorbed on mesoporous TiO_2 films.

β-CD. This suppression should be attributed to separation of porphyrin molecules by inclusion into the narrow cavity of CD, resulting in retarding the excitation energy hopping.

References

1 K. Kano, H. Kitagishi, M. Kodera, and S. Hirota, *Angew. Chem., Int. Ed.*, **44**, 435 (2005).
2 S. Hamai, *Bull. Chem. Soc. Jpn.*, **75**, 2371 (2002).
3 S. Hamai and T. Koshiyama, *J. Photochem. Photobiol., A*, **127**, 135 (1999).
4 X.-P. Wang, J.-H. Pan, and S.-M. Shuang, *Spectrochim. Acta, Part A*, **57**, 2755 (2001).
5 J. Mosinger, M. Deumié, K. Lang, P. Kubát, and D. M. Wagnerová, *J. Photochem. Photobiol., A*, **130**, 13 (2000).
6 X.-P. Wang, J.-H. Pan, S.-M. Shuang, and Y. Zhang, *Supramol. Chem.*, **14**, 419 (2002).
7 S. Hamai and T. Koshiyama, *Spectrochim. Acta, Part A*, **57**, 985 (2001).
8 X. Guo, W. An, S. Shuang, F. Cheng, and C. Dong, *J. Photochem. Photobiol., A*, **173**, 258 (2005).
9 Y. Lui, J.-H. Pan, Y.-L. Wei, and Y. Zhang, *Talanta*, **63**, 581 (2004).
10 B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991).
11 G. Benkö, J. Kallioinen, P. Myllyperkiö, F. Trif, J. E. I. Korppi-Tommola, A. P. Yartsev, and V. Sundström, *J. Phys. Chem. B*, **108**, 2862 (2004).
12 J. Kallioinen, G. Benkö, P. Myllyperkiö, L. Khriachtchev, B. Skårman, R. Wallenberg, M. Tuomikoski, J. Korppi-Tommola, V. Sundström, and A. P. Yartsev, *J. Phys. Chem. B*, **108**, 6365 (2004).
13 J. Kallioinen, G. Benkö, V. Sundström, J. E. I. Korppi-Tommola, and A. P. Yartsev, *J. Phys. Chem. B*, **106**, 4396 (2002).
14 Y. Fujii, Y. Tsukahara, and Y. Wada, *Bull. Chem. Soc. Jpn.*, submitted.
15 J. He, G. Benkö, F. Korodi, T. Polívka, R. Lomoth, B. Åkermark, L. Sun, A. Hagfeldt, and V. Sundström, *J. Am. Chem. Soc.*, **124**, 4922 (2002).
16 J.-J. Wu, H.-L. Ma, H.-S. Mao, Y. Wang, and W.-J. Jin, *J. Photochem. Photobiol., A*, **173**, 296 (2005).

Figure 2. ^{1}H NMR spectra of a D_2O solution of 5.0×10^{-3} M TPPS (a), a D_2O solution of 5.0×10^{-3} M TPPS containing 1.0×10^{-2} M HP-β-CD (b), and a D_2O solution of 5.0×10^{-3} M TPPS containing excess amount of HP-β-CD (c). The pH values of all D_2O solutions were adjusted at pH 10.