Fluorometric Detection of *p*-Chlorophenol by ZnTPP-Intercalated Dialkyl Ammonium Smectite

Takako Nagase,* Yukiko Takahasi, Toshishige M. Suzuki, Takeo Ebina, Yoshito Wakui, and Yoshio Onodera
Laboratory for Membrane Chemistry, National Institute of Advanced Industrial Science and Technology,
4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551

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Zn(II) tetraphenylporphyrin (ZnTPP)-intercalated dialkyl ammonium smectite was applied to the condensation and detection of chlorophenols in aqueous medium. ZnTPP and *p*-chlorophenol found to form a stable porphyrin-quinone dyad in micelles of dialkyl ammonium ion, accompanied with color-change and fluorescence quenching of ZnTPP. As a result, sub-ppm to ppm order of *p*-chlorophenol in water can be detected by the fluorescence quenching.

Pentachlorophenol and 2,4-dichlorophenol have been suspected as endocrine disrupters, and various detection methods have been investigated to monitor contaminations by these organohalides.[1–3] Both electrochemical and photochemical detection of organohalides have been investigated using metal-porphyrins in organic solvents.[2,3] Souza and Deviprasad synthesized Zn porphyrins, which can selectively detect quinones and hydroquinones by fluorescence quenching depend on a formation of porphyrin-quinhydrone complex.[3] Costa and Brookfield studied the interaction of Zn porphyrin in reversed micelles of benzyldimethyl-*n*-hexadecyl ammonium chloride.[4] However, the fluorescence sensitivity is not sufficient for the detection of organohalides in aqueous medium, presumably owing to the weak interaction between porphyrin and quinone.[3] On the other hand, clay minerals whose surface is modified with hydrophobic alkyl amines, are known to adsorb chlorophenols from aqueous medium.[5,6] Smectite, one of typical clay minerals, has negatively charged surface, and can favorably accommodate positively charged micelles composed of alkylamine molecules.[7] Since ZnTPP is hydrophobic,[8] we attempted to use dialkyl ammonium micelles for incorporation of ZnTPP into the interlayer space of smectite. This ternary composite system was applied to the condensation and fluorometric detection of chlorophenols in water.

Dialkyl ammonium chloride[9] was loaded on smectite[10] by mixing them in hot water. The amine content was in excess in terms of a cation exchange capacity of the smectite to synthesize a fully loaded organophilic smectite (H250HT). One mg of ZnTPP was mixed with 250 mg of H250HT in toluene to synthesize a compound (ZnTPP-H250HT).[11]

ZnTPP-H250HT powder was dispersed in various concentration of *p*-chlorophenol aqueous solutions at pH = 6–7 to study a photochemical change of ZnTPP-H250HT upon the addition of *p*-chlorophenol. After the reaction, the solid phase was filtrated and dispersed in ethanol to be a concentration of 0.2 wt%. The dispersion was allowed to stand for 2–3 min, and then the fluorescence emission spectrum and the UV-vis absorption spectrum were measured.

The measurement condition and the amount of *p*-chlorophenol adsorbed on 1 mg of adsorbent (CP_{ad}) are listed in Table 1. The CP_{ad} has increased obviously in the presence of ZnTPP compare to that in the absence of ZnTPP. The dispersion of 0.1 wt% ZnTPP-H250HT can be used to condensate ppm order of *p*-chlorophenol.

In the time-course of the UV spectral change of *p*-chlorophenol stirring with ZnTPP-H250HT in water, a new peak, attributed to quinone, appears at 245 nm[12] in conjugation with the attenuation of the peak at 224 and 280 nm of *p*-chlorophenol.[13] Since such a change is not observed in the dark or in the absence of ZnTPP, the formation of quinone described above can be attributed to the oxidation of *p*-chlorophenol with a photocatalytic participation of ZnTPP.[14]

ZnTPP-H250HT powder turns to be yellowish after the oxidation. Figure 1 shows the UV absorption spectra and the fluorescence emission spectra of 0.2 wt% ZnTPP-H250HT ethanol suspension. The absorption and the emission intensities corresponding to Soret band of ZnTPP apparently decrease with an increase in CP_{ad} value as shown in Figure 1, which suggests some interactions of porphyrin ring exist on the oxidation process of *p*-chlorophenol.[3,15]

The relationship between CP_{ad} and the attenuation in emission spectra follows the Stern-Volmer equation,[3]

$$Io/I - 1 = K\mathrm{sv}[\mathrm{Q}]$$

where *I*o is the peak intensity at 601 nm before the adsorption of *p*-chlorophenol, and *I* is that of after adsorption. [Q] is the content of quencher molecule corresponding to CP_{ad} and *K*sv is Stern-Volmer quenching constant (Figure 2).

The attenuation of absorption and emission peaks is also observed by quinone in place of *p*-chlorophenol after the reaction in the dark. It suggests that the formation of co-facial type porphyrin-quinone dyads takes place between ZnTPP and *p*-

Table 1. Adsorption of *p*-chlorophenol using dialkyl ammonium smectite in the absence (H250HT) and in the presence of ZnTPP (ZnTPP-H250HT)

Run No.	Adsorbent	Amount of Adsorbent /wt%	Init. Conc. of *p*-Cl phenol /ppm	CP_{ad}[a] /μmol mg⁻¹	Removal /%
1	H250HT	0.1	20.0	0.13	82 [b]
2	ZnTPP-H250HT	0.1	20.0	0.15	98 [b]
3		0.05	1.87	0.029	100 [c]
4		0.01	1.22	0.095	100 [c]
5		0.01	2.27	0.18	100 [c]
6		0.01	3.87	0.30	98 [c]

[a] Adsorption of *p*-chlorophenol per mg of adsorbent.
[b] Total Volume; 30 ml, Removal; Ten ml of the liquid phase was sampled after filtration, and 0.1 ml of 0.1 N HCl was added. Then, *p*-chlorophenol was extracted by 2 ml of ethylacetate settling for 24 h , and quantitatively analyzed by GC-MS.
[c] Total Volume; 50 ml, Removal of *p*-chlorophenol was determined from UV spectra of the liquid phase after filtration.

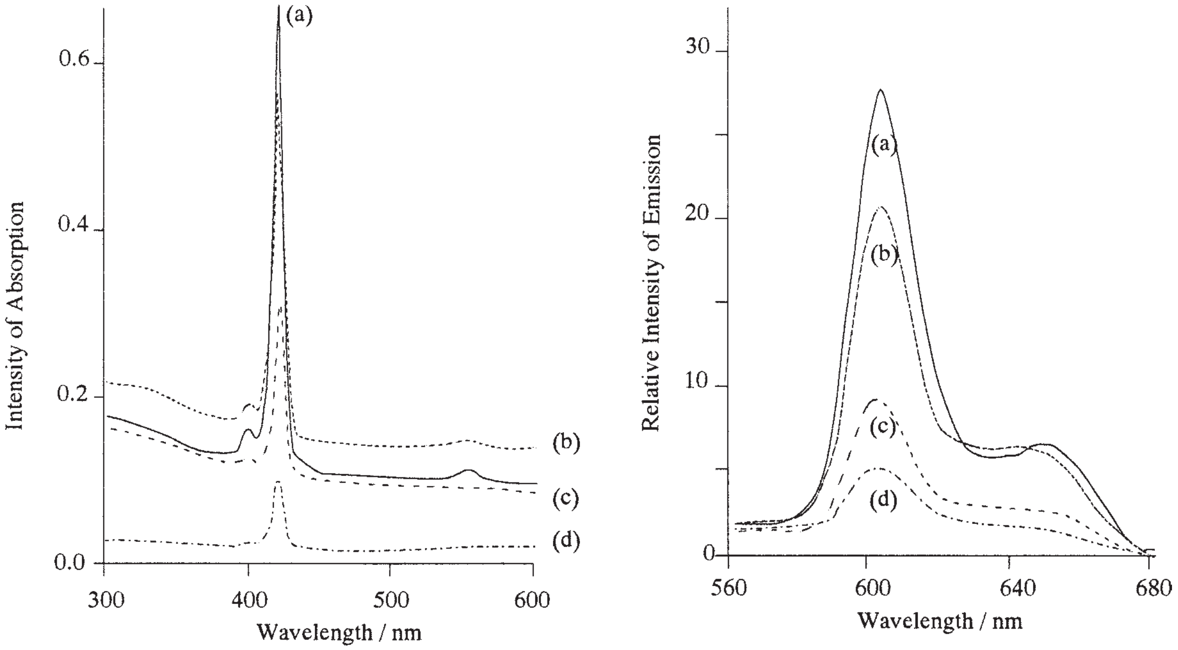

Figure 1. UV-vis absorption and fluorescense emission spectra of ZnTPP-intercalated dialkyl ammonium smectite (ZnTPP-H250HT) in ethanol suspension, before (a) and after adsorption (b)–(c). Each amount of adsorbed *p*-chlorophenol (CP_{ad}) is (b) 0.029, (c) 0.095, (d) 0.30 μmol/mg. $\lambda_{ex} = 400$ nm. Concentration of ZnTPP-H250HT in suspension is 0.2 wt%. Intensity of each spectrum decreases with increase in CP_{ad}.

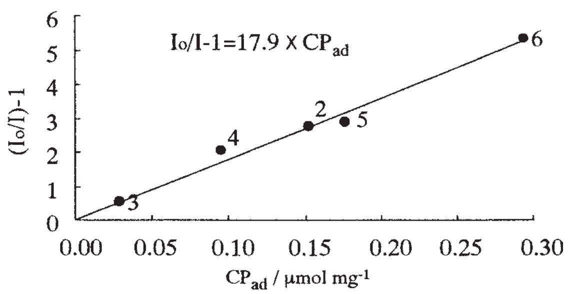

Figure 2. Relationship between adsorption of *p*-chlorophenol (CP_{ad}) and the fluorescence quenching at 601 nm in emission spectra of ZnTPP-intercalated dialkyl ammonium smectite in ethanol suspension. Concentration of ZnTPP in ethanol suspension is 6.2 μM. Numbers indicated run numbers listed in Table 1. The half quenching value of CP_{ad} is 0.056 μmol mg^{-1}.

chlorophenol.[15] This assumption is supported by FT-IR absorption bands at 3366–3377 and 3235–3240 cm^{-1} assigned to the internal hydrogen bonding of porphyrin-quinone dyads[3,15] appearing in the spectrum of dialkyl ammonium chloride upon the addition of quinone or *p*-chlorophenol in the presence of ZnTPP.[16]

No significant change in the emission intensity of ZnTPP-H250HT was observed upon direct addition of quinone or *p*-chlorophenol in ethanol. Therefore, the formation of porphyrin-quinone dyads is enhanced in the presence of the micelles in water, for this reason, the micelle-suspended smectite can condensate the porphyrin-quinone dyads into its interlayer space.

Since *K*sv of *p*-chlorophenol(17.9) was larger than that of quinone(12.7), some reactive intermediates may also concern with the attenuation. The emission intensity was decreased to one-half its initial value at $CP_{ad} = 0.056$ μmol/mg (Figure 2). Sub-ppm of *p*-chlorophenol can be detected using 0.1 wt% dispersion of ZnTPP-H250HT which yields detectable attenuation.[11]

In conclusion, ZnTPP-intercalated dialkylammonium smectite can assist the formation of stable porphyrin-quinone dyads in water owing to micelle formation in its interlayer spaces. This system can detect sub-ppm to ppm order of *p*-chlorophenol in water by fluorescence quenching. The result of this study also suggests the possibility of naked-eye detection of *p*-chlorophenol.

References and Notes

1 J. Burk, J. P. Conzen, B. Beckhaus, and H. J. Ache, *Sens. Actuators, B*, **18**, 291 (1994).
2 D. J. Dobson and S. Saini, *Anal. Chem.*, **69**, 3532 (1997).
3 F. D'Souza and G. R. Deviprasad, *J. Org. Chem.*, **66**, 4601 (2001). e.g., more than 30 mM of 1,4-benzoquinone is needed for 10% decrease in initial emission intensity of 20 μM ZnTPP.
4 S. M. B. Costa and R. L. Brookfield, *J. Chem. Soc., Faraday Trans. 2*, **82**, 991 (1986).
5 M. M. Mortland, S. Shaobai, and S. A. Boyd, *Clays Clay Miner.*, **34**, 581 (1986).
6 K. R. Srinivasan and H. S. Fogler, *Clays Clay Miner.*, **38**, 287 (1990).
7 T. Seki and K. Ichimura, *Macromolecules*, **23**, 31 (1990).
8 Solubility in water is under 0.8 ppm.
9 The dialkyl ammonium chloride contains 75% octadecyl, 24% hexadecyl, 1% octadecanyl groups as alkyl groups (Arquad 2HT-75 of Lion Akzo Co. Ltd.).
10 The smectite was synthesized hydrothermally at 250 °C for 2 h to have the composition of hectorite ($Na_{0.3}Mg_{2.7}Li_{0.}Si_4O_{10}(OH)_2$).
11 Obtained ZnTPP-H250HT has a absorption band at 423 nm in ethanol suspension, corresponding to Soret band of ZnTPP. However, the intensity of Soret band in the absorption spectrum of ZnTPP-H250HT is noticablly decreased compared to that of ZnTPP. The color changed from red-purple to bluish green. Peak intensities of both the absorption and fluorescence emission spectra linearly increased with an increase in the concentration of ZnTPP-H250HT ethanol suspension in the range of 0.1 to 0.4 wt%, and error was within 10%.
12 NIST (National Institute for Standards and Technology) Standard Reference Database 69- July 2001.
13 The time required to complete the reaction varied depending on the amount of adsorbent and concentration of *p*-chlorophenol. In the case of run 3, the peak at 224 nm was not recognized after 1.5 h, however, it took more than 45 h for complete disappearance of the peak in the condition of run 6.
14 R. S. Shukla, A. Robert, and B. Meunier, *J. Mole. Catal. A*, **113**, 45 (1996).
15 T. Hayashi, T. Miyahara, N. Koide, Y. Kato, H. Masuda, and H. Ogoshi, *J. Am. Chem. Soc*, **119**, 7281 (1997).
16 For comparison with ZnTPP-H250HT, a compound consisting of ZnTPP and dialkyl ammonium chloride was also prepared by mixing them in toluene in the absence of smectite.