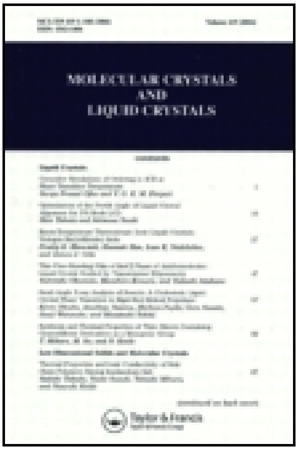

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Optochemical HCl and Cl_2 Gas Detection Based on Tetraphenylporphin Dispersed in Ethylcellulose

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OPTOCHEMICAL HCl AND Cl_2 GAS DETECTION BASED ON TETRAPHENYLPORPHIN DISPERSED IN ETHYLCELLULOSE

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Abstract To detect sub-ppm levels of HCl gas, spectral changes of tetraphenylporphine and derivatives dispersed in ethylcellulose were examined in the visible region. For free base tetraphenylporphyrin, the absorbance at 450 nm and 670 nm is sensitive to sub-ppm levels of HCl and also a good reversibilty is observed at room temperature. The Soret and Q-bands are insensitive to NH_3, Cl_2, NO_2 and NO at room temperature. For zinc tetrabromotetraphenylporphine, the absorbance at 479 nm and 722 nm is sensitive to sub-ppm levels of HCl gas and also good reversibilty is observed at room temperature.

INTRODUCTION

To control the emission of gaseous pollutants such as sulfur oxide, nitrogen oxide and other toxic gases, analytical instruments are needed which measure the concentration of these compounds. Chemical sensors offer a promising and inexpensive way to fulfill this analytical task. Recently to measure concentrations in the order of ppm or ppb of these compounds, various optochemical sensors workable at room temperature have been presented.[1-8] Many pronounced interactions between conjugated organic compounds and gases may be classified in terms of irreversible chemical attack or reversible chemical reaction. These can lead to the generation of detectable changes in physical properties of organic compounds including semiconductivity, photoconductivity, visible absorption spectra and infrared spectra. Especially for phthalocyanines and porphyrins which planar conjugated macrocyclic nitrogenous bases, conductivity and/or spectral behavior are very sensitive to the presence of toxic gases.[9-12] Since they are very stable both thermally and chemically, they have attracted much interest as potential materials to be integrated in resistive-type and in optochemical-type gas sensors. It is expected that for free base tetraphenylporphine dispersed in polymer matrices, the agglomeration with porphine molecules can be depressed (weaken the plane-plane interaction between porphine molecules) and the tetrapyrrolic macrocycle is oxidized in successive monoelectronic steps giving monocationic radicals and dications or forms acid salts by exposure to HCl. The introduction of phenyl groups into *meso*-positions is effective to protect nitration or chlorination of *meso*-positions. Furthermore, bromination makes the oxidation of the porphine ligand more difficult and induces red shifts of the Soret and Q-bands.

Recently, it is desired to detect sub-ppm levels of HCl in exhausted gases. In the present work optical properties of immobilized tetraphenylporphine and zinc tetraphenyl porphine were examined with respect to application for detection of sub-ppm levels of HCl.

EXPERIMANTAL

Chemicals:

The studied porphyrins, prepared according to known procedures were free base tetraphenylporphine ($TPPH_2$), free base tetrabromotetraphenyl- porphine (Br_4TPPH_2), free base octabromotetraphenylporphine (Br_8TPPH_2) zinc tetraphenylporphine (TPPZn), zinc tetrabromotetraphenylporphine (Br_4TPPZn) and zinc octabromotetraphenylporphine (Br_8TPPZn).[13-15] Some of them were also obtained from Aldrich Chemicals and Tokyo Kasei. Ethylcellulose (EC) was obtained from Aldrich Chemicals. Porphyrins and EC were dissolved in a mixture of toluene and ethanol. The solutions were used to prepare films by coating on alumina substrates or quartz plates. Afterwards the films were heated at 60 ℃ *in vacuo* to remove the solvent.

Optical measurements:

The spectra of the element formed on alumina plates were measured in reflection mode. Filtered light from a D_2/I_2 lamp (400 nm ~ 800 nm) was guided into a fiber and the collected/reflected light was analyzed using a spectro multichannel photodetector (MCPD-1000, Otsuka electronics). The spectrum (I_0) of the element in nitrogen was measured first and used as a reference for measuring the spectrum (I/I_0) of the film. The reflectance(%) was defined as $100xI/I_0$. All measurements were performed at 30 °C. Standard gases (HCl, Cl_2, NO_2, NO and NH_3) diluted with nitrogen were obtained from Sumitomo seika. The concentration was controlled by mixing standard gas with nitrogen.

RESULTS AND DISCUSSION

Free base tetraphenylporphines:

It is well known that in nonaqueous media the tetrapyrrolic macrocycle of the porphine is oxidized in successive monoelectronic steps giving monocationic radicals and dications. The reduction of the tetrapyrrolic ring leads, by a similar mechanism, to monoanionic radicals and to a dianion. Oxidation/reduction behavior is affected by the electronegativity of the porphine ring which is influenced by the β-substituent. In general, electron-withdrawing substituents make the oxidation of the porphine ligand more difficult. Furthermore, the amphoteric nature of the porphine molecule permits the formation of acid salts involving the addition of protons to the center of the porphine. In 1951, Dorough et.al.[16] reported that the amphoteric nature of the porphine molecule permits the formation of acid salts involving the addition of protons to the center of the porphine and the spectra of these salts are influenced by the nature of the acid. Structually the porphine nucleus (P) can be regarded as a polyvalent ampholyte with all four nitrogen atoms possible basic centers and the two pyrrole type (>NH) nitrogen atoms possible acidic centers. Under normally attainable pH conditions the porphine nucleus would behave as a tetravalent ampholyte having two basic and two acidic centers namely, P^{2-}, PH^-, PH_2, PH_3^+, PH_4^{2+}.[17] Apparent dissociation constants of TPP in nitrobenzene, titrated with perchlolic acid in dioxane have been reported to $4.2x10^{-5}$ and $14x10^{-5}$ for $TPPH_3^+ \rightleftarrows TPPH_2 + H^+$ and $TPPH_4^{2+} \rightleftarrows TPPH_3^+ + H^+$, respectively, by Aronoff.[18] Bhyrappa and Krishnan [15] suggested that the imino nitrogens of Br_8TPPH_2 are relatively less basic than those of $TPPH_2$. The acidic nature of Br_8TPPH_2 possibly arises from the electron-withdrawing substituents (bromine) at the pyrrole carbons.

Firstly, absorption spectra of EC composite and of DMF solution of Br_xTPPH_2 are examined. The Soret band (λ_{max} = 416 nm) with a shoulder at 400 nm and the Q-bands (λ_{max} = 515, 549, 590 and 646 nm) were observed DMF solution ($5x10^{-6}$ mol/l), in addition, fluorescence with λ_{max}=650 nm was also observed. By adding conc. HCl to the solution, the intensity of the fluorescence decreases and enhancement of the absorbance at λ_{max}=656 nm and red-shift (from 416 nm to 448 nm) of the Soret band are observed by an adding of conc. HCl to the solution. An adding of HCl results in the formation of dicationic salt.

Absorption spectrum is influenced by the $TPPH_2$ concentration (Fig.1). For the film with $1x10^{-5}$ mol/gEC, the Soret band is observed at 416 nm with a shoulder at 400 nm. A half-width of the Soret band is not so different from that for the DMF solution

(5×10^{-6} mol/l) *i.e.* the plane-plane interactions between porphine molecules are not considerable. With increasing the concentration, the Soret band is splitted and λ_{max} is observed at 414 and 419 nm with the shoulder. A detailed study is required to resolve several explanations of these observations, *e.g.*, concentration-dependent aggregation (sandwich-type or in-plane interaction).

The λ_{max} of the Soret band was red-shifted with an increase in the number of bromine substituents at the pyrrole position. For Br_4TPPH_2 film (1×10^{-5} mol/gEC), the Soret band is observed at 438 nm and the Q-bands at 538, 622 and 696 nm. While the observed λ_{max} of Soret and Q-bands are slightly different from the results for dichloromethane solution,[12,14] the shapes of the observed spectra are very similar to the results of dichloromethane solution.

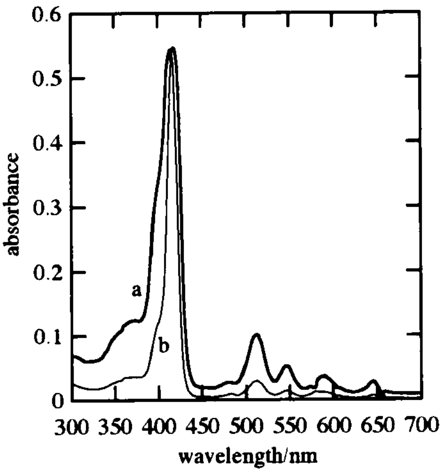

Fig.1. Spectral changes with TPP concentration of EC-composite film. TPP/EC; a) 6.3×10^{-5} mol/g, b) 1.6×10^{-5} mol/g.

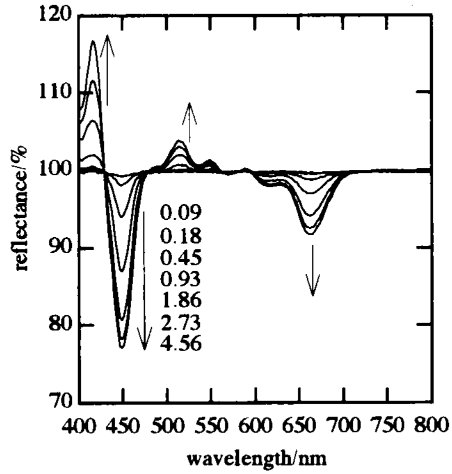

Fig.2 Spectral changes of TPP/EC with HCl. TPP/EC;2.6×10^{-5} mol/g
HCl concentration in ppm is shown in the figure.

When HCl gas was introduced into the chamber, the spectrum responses to the presence of HCl. The spectral changes with HCl introduction are shown in Fig.2. The reflectance at λ_{max} = 450, 618 and 664 nm decreases and the reflectance at λ_{max} = 414, 548, 594 nm increases with an increase in the concentration of HCl gas. These changes are reversible and when HCl was cut off, the spectrum returned completely. The recovery time is prolonged when a higher concentration of HCl gas is passed thorough the cell. The spectral changes with HCl are explained by the formation of cationic salt. As a cationic salt, mono- and di-cation is considered. While the dissociation constant of

$TPPH_2$ in EC matrix is not determined, it seems that the exposure to HCl induces the formation of dicationic salt since the dissociation constants in the solution are very small as described above.

For the film with a higher $TPPH_2$ content the spectral changes with HCl exposure are slightly different especially in a higher HCl concentration (> 1 ppm), *i.e.*, additional new bands which sensitive to the HCl are observed at λ_{max} = 474 and 720 nm as shown in Fig.3. The absorption bands appeared at 474 nm and 720 nm are observed for the film containing $3x10^{-5}$ mol/gEC or higher and when a higher concentration of HCl (> 1 ppm) is exposed. A critical concentration of HCl in which the appearances of the absorption bands at 474 nm and 720 nm have a tendency to increase with a decrease in the $TPPH_2$ content of the film. The observed dependency is applicable to a warning element to detect a critical concentration of HCl. These observations may be related to the existence of aggregated forms of $TPPH_2$. A more detailed study is required to realize these observations.

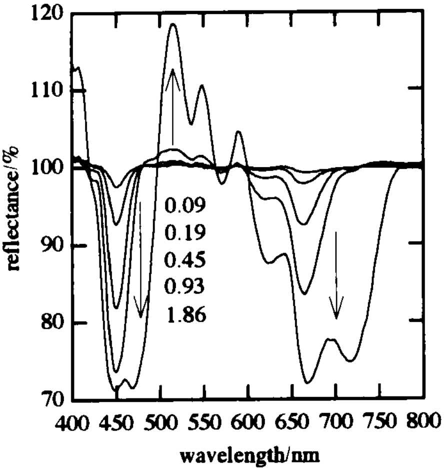

Fig. 3. Spectral changes of TPP/EC with HCl.
TPP/EC; $13.3x10^{-5}$ mol/g.
HCl concentration in ppm is shown in the figure.

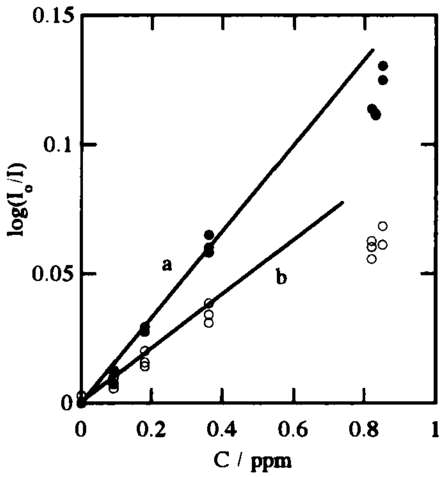

Fig.4. Concentration dependence of $\log(I_0/I)$ of the Soret band.
a) $TPPH_2$, b) Br_4TPPH_2.

The $\log(I_0/I)$ corresponding to absorbance is proportional to HCl concentration in the range of sub-ppm levels (below 1 ppm) as shown in Fig. 4. For the exposure to 1 ppm of NH_3, Cl_2, NO_2 or NO/N_2, any valuable spectral changes in the range between 400 nm and 800 nm could not be observed for the composite films.

To modify λ_{max} of the band sensitive to HCl, the brominated TPP was also examined. As mentioned above, the λ_{max} of the Soret and Q-bands can be red-shifted by the bromination. For the composite with Br_4TPPH_2, the reflectance at 436 nm corresponding to the Soret band increased with increasing HCl concentration and the reflectance at 479 and 725 nm decreased. Similar spectral changes were also observed for Br_8TPPH_2 while the λ_{max} of each band had a longer wavelength (increase in the reflectance at 467 nm and decrease in the reflectance at 499 and 738 nm with HCl).

Zinc tetraphenylporphines:

The Soret band with λ_{max} = 425 nm is detected for the DMF solution of TPPZn. The λ_{max} of the Soret band was red-shifted with an increase in the number of bromine substituents at the pyrrole position (λ_{max} = 436 nm for Br_4TPPZn and λ_{max} = 476 nm for Br_8TPPZn). When HCl gas was introduced, the spectrum of the Br_4TPPZn composite film responses to the presence of HCl. The spectral changes with HCl introduction are shown in Fig. 5. The reflectance with λ_{max} = 479 and 722 nm decreases with an increase in the concentration of HCl gas. These changes are reversible and when HCl was cut off. When the sample is exposed to nitrogen flow Br_4TPPZn exists in the neutral form. By exposure to HCl gas the formation of the acid salt may proceed. In Fig. 6, the reflectance changes at 479 nm and 722 nm for HCl concentration changes between 0 ppm and 5 ppm are shown. A fast response behavior and good reversibility

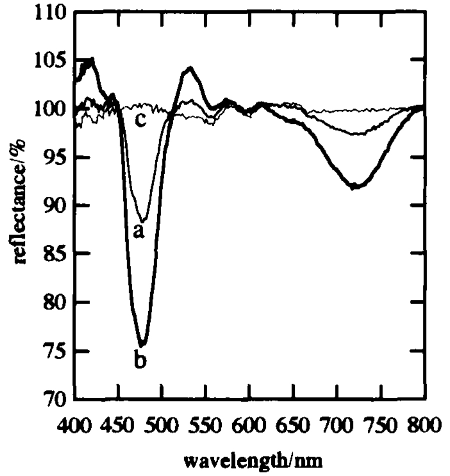

Fig. 5. Spectral changes with HCl of Br_4TPPZn. a)0.5ppm, b)5ppm, c)N_2 after exposed to 5ppmHCl.

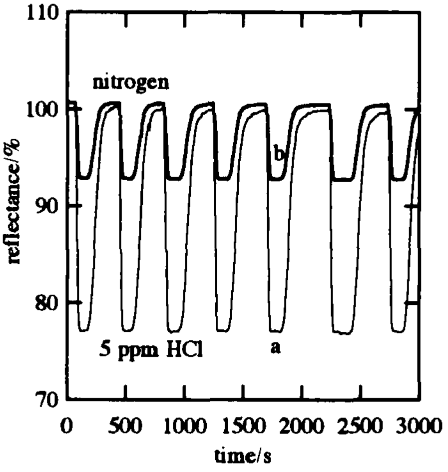

Fig. 6. Response behavior of Br_4TPPZn film. a) 479 nm, b) 722 nm.

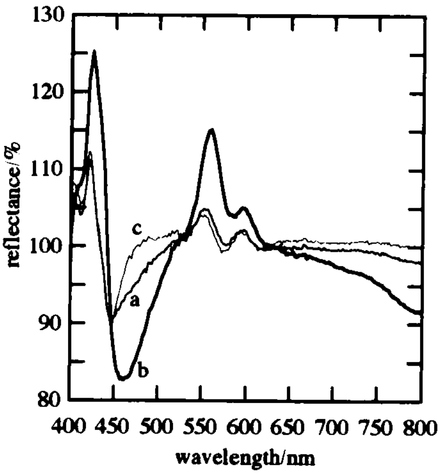

Fig.7. Spectral changes with Cl_2 of TPPZn film.
a) 0.5ppm b) 5ppm, c) N_2 after exposed to 5 ppm Cl_2.

are observed. Furthermore, from the calibration curves it is expected that the film is applicable to detect 0.5 ppm HCl or less. For the composite with TPPZn, any apparent spectral changes in the region of 400 nm and 800 nm were not detected when HCl concentration was changed from 0 ppm to 5 ppm, and for Br_8TPPZn the reflectance at 503 nm and 739 nm only slightly decreased (about 3 %). The effect of the degree of bromination on the HCl sensitivity may be caused by the difference of distortion of the macrocycle ring.

The spectrum of the TPPZn film is influenced by Cl_2 gas and the results are shown in Fig. 7. When 5 ppm Cl_2 was passed through, the reflectance at 425, 558 and 596 nm increased and that at 463 nm and 790 nm decreased. After a cut of the Cl_2 gas, the spectrum c (in Fig.7) was observed, *i.e.*, the reflectance at 425 nm and 800 nm recovered slightly while the reflectance at 445 nm remains. A similar behavior is also observed for Br_4TPPZn and Br_8TPPZn where these changes are observed at longer wavelengths. The absorption spectra of TPPZn and its cation radical in CH_2Cl_2 were reported.[19] The reported spectral changes caused by the formation of the cation radical are very similar to the results observed for the TPPZn film. In this work, the formation of the cation radical of TPPZn was not examined by using other techniques such as ESR but the spectral changes by Cl_2 are interpretable in terms of the formation of the cation radical of TPPZn. The spectrum of Br_xTPPZn is very sensitive to Cl_2 but no good recovering behavior is confirmed at room temperature.

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