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Optochemical HCl gas sensor using substituted tetraphenylporphine–ethylcellulose composite films

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Composite films of various tetraphenylporphines embedded in ethylcellulose were prepared and their optical response to gaseous HCl was investigated. The absorbance of the Soret and Q-bands for free-base tetraphenylporphines is reversibly sensitive to ppm levels of HCl. The replacement of the *para* hydrogen in one phenyl group with a hydroxy group is effective in enhancing the sensitivity of the Q-band region while prolonging response time. In addition, the temperature coefficient of the sensitivity of $TP(OH)(R)_3PH_2$ is lower than that of $TPPH_2$. Under filtered light (>600 nm) a significant deterioration of the sensitivity was not observed for more than 50 d.

Recently, various optochemical sensors operating at room temperature have been reported to measure the emission of gaseous pollutants at ppm or ppb concentration levels.[1–8] It is well known that in nonaqueous media the tetrapyrrolic porphine macrocycle is oxidized in successive monoelectronic steps giving monocationic radicals and dications. Furthermore, the amphoteric nature of the porphine molecule permits the formation of acid salts involving the addition of protons to the porphine center.

Recently, there has been a need for the detection of sub-ppm levels of HCl gas concentrations from adsorbing towers in semiconductor factories. Given that the environmental standard for HCl gas is 5 ppm, in the present work, the optical properties of immobilized substituted tetraphenylporphines were examined for their potential use in the detection of such levels of HCl gas. Furthermore, we also discuss the effects of substituents on sensitivity, response behavior and long term stability.

Experimental

Chemicals

Synthesis of 5-(*p*-hydroxyphenyl)-10,15,20-tris(*p*-alkylphenyl)porphine [$TP(OH)(R)_3PH_2$] **1–3**.

The general method was modified by Adler *et al.*[9] as follows: *p*-hydroxybenzaldehyde (12 mmol), *p*-alkylbenzaldehyde or *p*-alkoxybenzaldehyde (36 mmol) in propionic acid (150 cm^3) was stirred and slowly heated to 80 °C until the *p*-hydroxybenzaldehyde dissolved. Pyrrole (50 mmol) was slowly added to the above solution and heated at 150 °C, then the reaction mixture was refluxed for 70 min and allowed to cool overnight. Ethanol (150 cm^3) was added to the dark propionic acid residues under vigorous stirring at room temperature for 30 min, then the residue was filtered through a sintered funnel and washed with ethanol until the filtrate became clear. The violet solid obtained was dissolved in chloroform (150 cm^3), washed with saturated aqueous sodium carbonate (3×50 cm^3), and dried over anhydrous sodium sulfate. After solvent evaporation, the purple needles obtained were chromatographed on alumina, and eluted with dichloromethane (DCM)–*n*-hexane (4:1). The first band off the column was the 5,10,15,20-tetrakis(*p*-alkylphenyl)porphine by-product. The third band, which moved very slowly, was eluted with DCM containing ethanol (1%, gradually increasing to 3%) and collected and concentrated. For further purification, each component was subjected to column chromatography on silica gel, and eluted with DCM containing ethanol (0.5%, gradually increasing to 5%). Compounds **1–3** were isolated, then recrystallized from DCM–methanol–*n*-hexane and identified as follows:

5-(*p*-Hydroxyphenyl)-10,15,20-triphenylporphine 1. Yield 3.5%, purple crystals, mp>300 °C. R_f, 0.43 (DCM). UV–VIS($CHCl_3$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 417 (490 000), 514 (19 000), 549 (9300), 591 (5900), 645 (5400). δ_H ($CDCl_3$) 8.80 (s, 8H, pyrrole β-H), 8.17 (m, 6H, aromatic H), 7.70 (m, 7H, aromatic H), 7.23 (m, 4H, aromatic H). MS(FAB) *m*/*z*: 631.2 ($M+H^+$).

5-(*p*-Hydroxyphenyl)-10,15,20-tris(*p*-*tert*-butylphenyl)porphine 2. Yield 2.9%, purple crystals, mp>300 °C. R_f, 0.47 (DCM). UV–VIS($CHCl_3$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 420 (570 000), 517 (20 000), 554 (12 000), 592 (5800), 649 (7100). δ_H ($CDCl_3$) 8.85 (s, 8H, pyrrole β-H), 8.10 (m, 10H, aromatic H), 7.76 (m, 4H, aromatic H), 7.20 (m, 2H, aromatic H), 1.60 (s, 27H, Bu^t). MS(FAB) *m*/*z*: 799.4 ($M+H^+$). Anal. calc. for $C_{56}H_{54}N_4O$ (798.4): C, 84.17; H, 6.82; N, 7.02. Found: C, 84.21; H, 6.80; N, 7.01%.

5-(*p*-Hydroxyphenyl)-10,15,20-tris(*p*-octyloxyphenyl)porphine 3. Yield 2.8%, purple crystals, mp>300 °C. R_f, 0.52 (DCM). UV–VIS($CHCl_3$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 423 (550 000), 515 (21 000), 555 (15 000), 593 (6400), 651 (9700). δ_H ($CDCl_3$) 8.90 (s, 8H, pyrrole β-H), 8.05 (d, 6H, aromatic H), 7.97 (m, 2H, aromatic H), 7.87 (m, 6H, aromatic H), 7.50 (d, 6H, aromatic H) 7.08 (m, 8H, aromatic H), 4.10 (t, 6H, $-O-CH_2-$), 2.0 (m, 6H, $-CH_2-$), 1.60–1.30 (br m, 30H, $-CH_2-$), 0.90 (t, 9H, $-CH_3$). MS(FAB) *m*/*z*: 1015.6 ($M+H^+$).

Tetraphenylporphine (chlorin free) ($TPPH_2$), and 5,10,15,20-tetrakis(*p*-hydroxyphenyl)porphine [$TP(OH)PH_2$] were obtained from Aldrich Chemicals and Tokyo Kasei. The molecular structures of the porphines are shown. Ethylcellulose (EC) was obtained from Aldrich Chemicals. Porphines and

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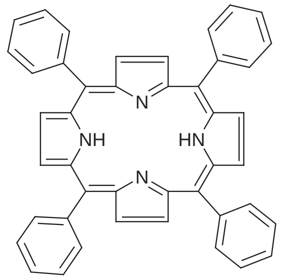
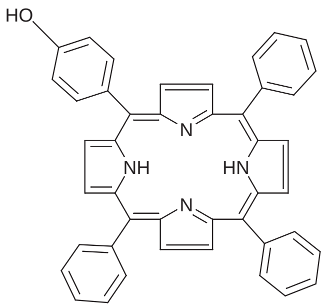
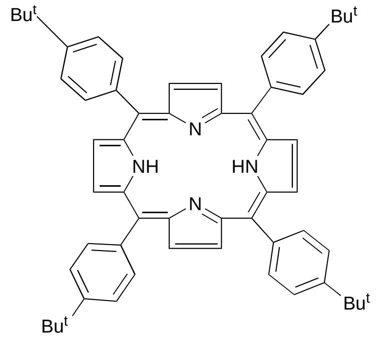
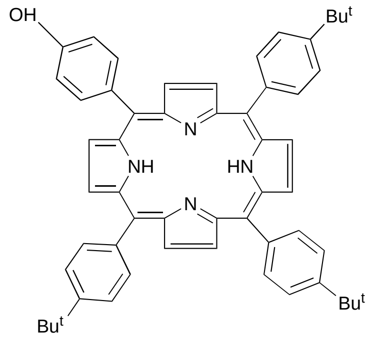

tetraphenylporphine (TPPH$_2$)


5-(*p*-hydroxyphenyl)-10,15,20-triphenylporphine
[TP(OH)(H)$_3$PH$_2$]


5,10,15,20-tetrakis(*p*-*tert*-butylphenyl)porphine
[TP(Bu^t)PH$_2$]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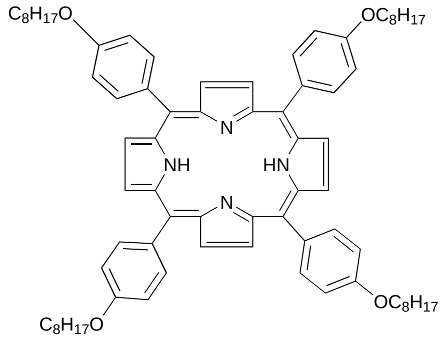
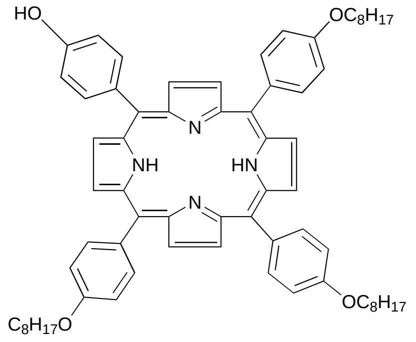
[TP(OH)(Bu^t)$_3$PH$_2$]


5,10,15,20-tetrakis(*p*-octyloxyphenyl)porphine
[TP(OC)PH$_2$]


5-(*p*-hydroxyphenyl)-10,15,20-tris(*p*-octyloxyphenyl)porphine
[TP(OH)(OC)$_3$PH$_2$]

EC were dissolved in a mixture of toluene, ethanol and bis(2-ethylhexyl) phthalate (DOP) as a plasticizer. In the previous work,[10] the absorption spectra of the EC-composite were examined for TPPH$_2$ and TP(OH)PH$_2$. The half width of the Soret band increases with porphine content indicating intermolecular interactions, *e.g.* concentration dependent aggregations. A large proportion of the porphine results in formation of inhomogeneous films containing some porphine crystals. For the films containing 5×10^{-5} mol g^{-1} of EC or less, the half width of the band remains a constant, and smooth, homogeneous films are obtainable. To obtain reproducible characteristics, the films on alumina and/or quartz substrates from solutions of concentration 5×10^{-5} mol (g EC)$^{-1}$ or less were prepared with a spinner. The films were heated at 60 °C *in vacuo* to remove the solvent.

Optical measurements

The spectra of the thin films ($\sim$5 μm) deposited on alumina plates were measured in reflection mode. Filtered light from a D$_2$/I$_2$ lamp (400–800 nm, 15 W) was guided into a fiber and the reflected light was collected and analyzed using a multichannel spectrophotodetector (MCPD-1000, Otsuka electronics). The spectrum (I_0) of the composite film was first measured in nitrogen and used as a reference for measuring the spectrum (I/I_0) of the film in other environments. The reflectance (%) is defined as 100 I/I_0. Standard dry gases (HCl, Cl$_2$, NO$_2$ and NO) diluted with nitrogen were obtained from Sumitomo Seika. The concentration was controlled by mixing the standard gas with nitrogen.

Results and Discussion

The absorption spectra in the UV–VIS region of free base tetraphenylporphines have been extensively documented for thin solid films and solutions. These spectra all consist of a very strong band around 420 nm (the Soret band) and four moderately strong bands (Q-bands) in the 500–650 nm region. It is well known that in nonaqueous media the porphine macrocycle is oxidized in successive monoelectronic steps giving monocationic radicals and dications. Carnieri and Harriman[11] have reported that radical π-cations are very unstable in solution, being oxidized to the π-dications by

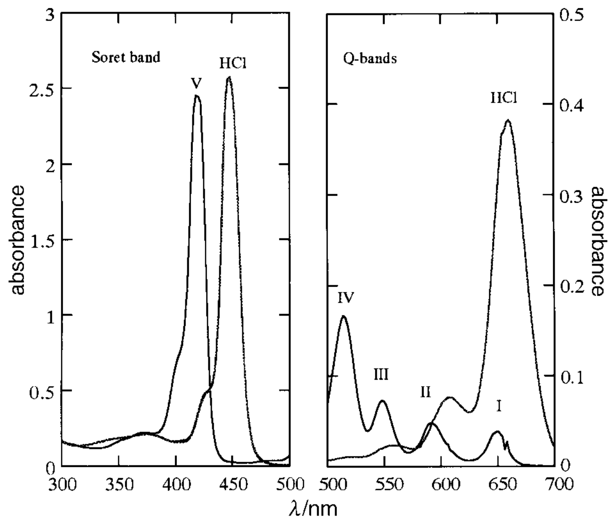


Fig. 1 Absorption spectra of $TPPH_2$-benzene solution with and without HCl

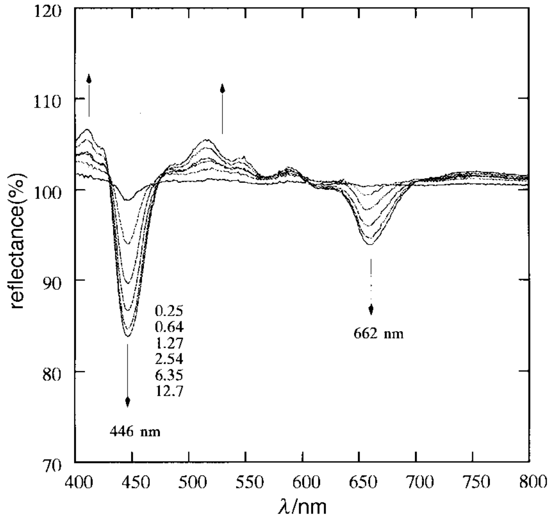
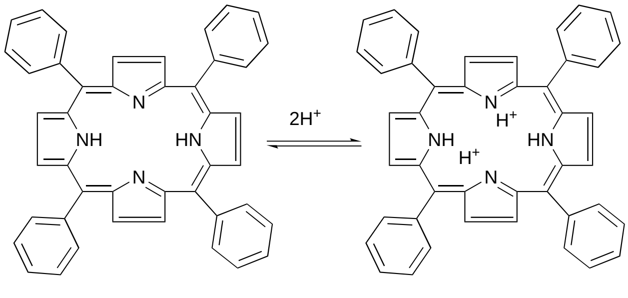


Fig. 2 Spectral changes of $TPPH_2$–EC composite without DOP upon exposure to HCl gas at 30 °C. $TPPH_2$: 5×10^{-5} mol per g EC. HCl concentrations in ppm are shown.

electron loss. Furthermore, as reported in 1951 by Dorough *et al.*,[12] 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 optical absorption spectra of these salts are influenced by the nature of the acid. The porphine nucleus can be regarded structurally as a polyvalent amphotyte or ampholite because all four nitrogen atoms are potential basic centers and the two pyrrolic type (=NH) nitrogen atoms are possible acidic centers.

Absorption spectra of $TPPH_2$–benzene solutions (5×10^{-5} mol cm^{-3}, 5 cm^3) with and without conc. HCl, HNO_3 and HF solution (5×10^{-4} cm^3) were measured. For the benzene solution, the Soret band is at 446 nm for HCl, 439 nm for HNO_3 and 435 nm for HF. The result for HCl is shown in Fig. 1. From these spectra, one can note that the spectral pattern changed upon addition of HCl; the four Q-band spectrum, indicating D_{2h} symmetry for free-base porphine, changed to a two Q-band spectrum, indicating D_{4h} symmetry. The change in the spectra upon addition of HCl can be attributed in general to the attachment of protons (diprotonation) to two imino nitrogen atoms of the pyrroline-like ring in the free-base.

A similar spectral change is expected for the EC composite film. When dry HCl gas was introduced into the chamber, the spectral response to HCl concentration changes is as shown in Fig. 2 for the DOP free film containing 5×10^{-5} mol g^{-1} of EC of $TPPH_2$. The reflectance at $\lambda_{max}=446$ and 662 nm decreased and some isosbestic points were detected. These changes were reversible. These results are very similar to the changes observed upon diprotonation of $TPPH_2$ (Scheme 1). Fig. 3 shows the percent reflectance changes of $TPPH_2$–EC composite at $\lambda_{max}=446$ nm during exposure to nitrogen and 12 ppm HCl. The response and recovery times became shorter with increase in working temperature, while the degree of the changes/sensitivity became smaller. The doping with DOP was effective for improving the response behavior without affecting the λ_{max} values. The response behavior was examined for a $TPPH_2$–EC composite containing DOP. The doping resulted in an enhancement of the sensitivity at the Soret and Q(0–0)-band; both the response and recovery time became shorter, as shown in Fig. 4. For free-base tetraphenylporphine, the absorbance of the Soret and Q-bands was reversibly sensitive to ppm levels of HCl at room temperature. Some fading was detected for specimens exposed to light from a 50 W xenon lamp for 3 h. Irradiation with light from a D_2/I_2 lamp (15 W) resulted in some deterioration of the sensitivity, indicating a lack of long-term stability. The sensitivity changes of the Soret band under near-UV–VIS (400–800 nm) continuous irradiation for $TPPH_2$–EC composite containing DOP were examined, confirming that the sensitivity was halved after 30 d as shown in Fig. 5. To improve long-term stability, the use of near-UV-cut light was considered. Under irradiation with filtered light (> 600 nm), a marked deterioration of the sensitivity was not observed for more than 50 d.



Scheme 1 Protonation process

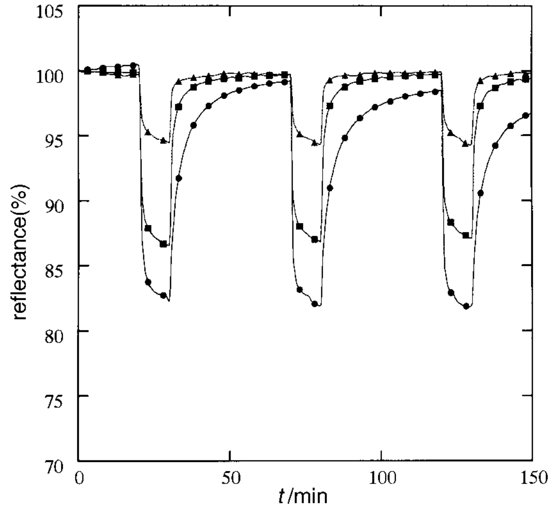


Fig. 3 Response behavior of $TPPH_2$–EC composite film without DOP at 446 nm. HCl concentration is changed from 0 ppm (nitrogen) to 12.7 ppm and the reflectance measured again. (●) 30 °C, (■) 45 °C and (▲) 60 °C.

To maintain long-term stability, operation in a longer wavelength region (> 600 nm) is preferable while the molar absorp-

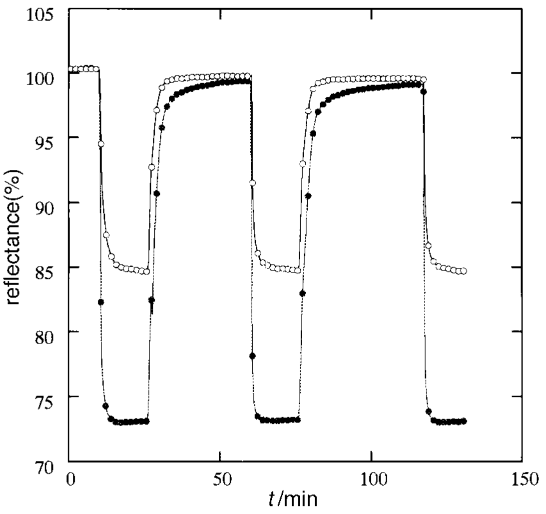


Fig. 4 Reflectance changes at 448 nm (●) and 662 nm (○) of $TPPH_2$–EC composite film at 40 °C. $TPPH_2$: 2.5×10^{-5} mol per g EC with DOP HCl concentration is changed from 0 ppm (nitrogen) to 12.7 ppm and the reflectance measured again.

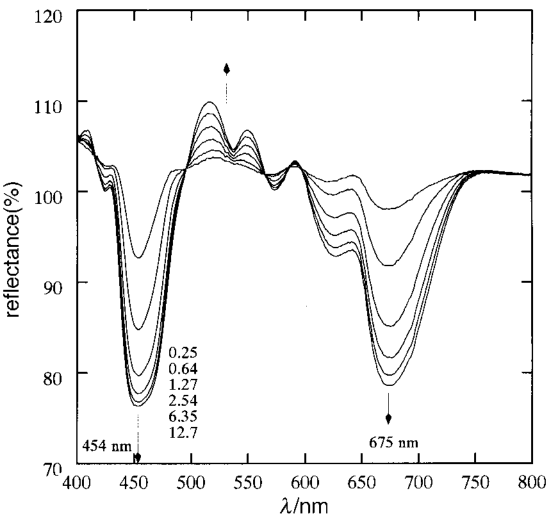


Fig. 6 Spectral changes of $TP(OH)(H)_3)PH_2$–EC composite upon exposure to HCl gas at 30 °C. $TP(OH)(H)_3PH_2$: 5×10^{-5} mol g per EC. HCl concentrations in ppm are shown.

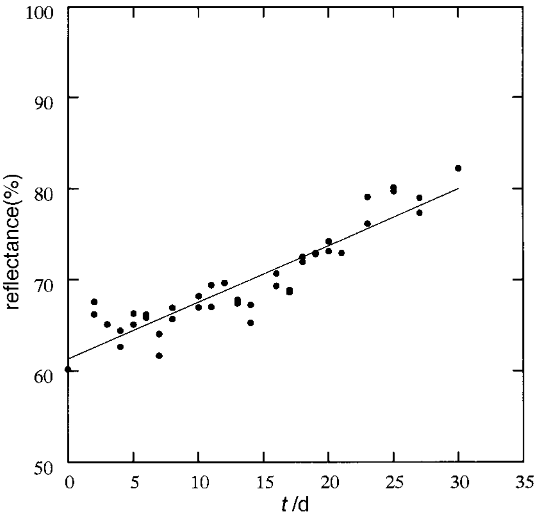


Fig. 5 Change of the sensitivity to 10 ppm HCl of $TPPH_2$–EC composite with DOP at 30 °C. During the measurement, the composite was exposed continuously to light.

tion coefficient of the Q-band is about tenfold lower than that of the Soret band for the acid dication form of $TPPH_2$. For $TPPH_2$–EC composites, introducing 0.1 ppm HCl resulted in a decrease of only about 2% in reflectance at 662 nm [Q(0–0) band]. To improve sensitivity, the use of $TPPH_2$ derivatives having a higher molar absorption coefficient at the Q-band is desirable. Acid dications showed an enhanced bathochromic shift relative to the *meso*-tetraphenylporphine itself. Thus the molar absorption coefficient of the Q(0–0) band appeared in a longer wavelength region (> 650 nm); the larger the shift, the larger the electron donating power of the substituents. Meot-Ner and Adler[13] reported that an increase in the electron-donating power of the *para* substituents results in a red shift of all the observed peaks for both free-base and dication forms with an increase in the oscillator strength. It seems that the oscillator strength increases monotonically with the λ_{max} of peak I [Q(0–0) band] for both free-base and dicationic forms.

These results suggested to us that the substitution of the hydrogen *para* to the phenyl group with an electron donating substituent, such as hydroxy, is suitable to improve and enhance sensitivity in the Q(0–0) band region. Furthermore, it is expected that the HCl sorption ability may be enhanced by the presence of the phenolic hydroxy group. In previous work,[10] the spectral changes with time of 5,10,15,20-tetrakis(*p*-hydroxyphenyl)porphine–EC composite upon exposure to 0.09 ppm of dry HCl gas were examined. Exposure to 0.09 ppm HCl resulted in a gradual decrease in the percent reflectance at about 455 and 710 nm with blue-shifts. The response time was extremely long compared to that for $TPPH_2$–EC composites. The recovery time was also long, *e.g.* the specimen must be held in pure nitrogen for 3 d or more at room temperature to recover the initial state. The sensitivity of the Q(0–0) band was very high and reversible when the blue-shifts were detected. The response behavior and the sensitivity may be influenced by the number of *p*-hydroxyphenyl groups, so we synthesized and examined substituted tetraphenylporphines.

In dimethylformamide (DMF) solution, λ_{max} of the Soret- and Q(0–0)-bands of the neutral form are 416 and 647 nm for $TPPH_2$, 418 and 649 nm for $TP(OH)(H)_3PH_2$, 422 and 653 nm for $TP(OH)(H)_3PH_2$, 419 and 651 nm for $TP(Bu^t)PH_2$, 420 and 651 nm for $TP(OH)(Bu^t)_3PH_2$, 421 and 651 nm for $TP(OC)PH_2$, 422 and 651 nm for $TP(OH)(OC)_3PH_2$, respectively. For the DMF solution with conc. HCl, λ_{max} values of the Soret- and Q(0–0)-band of the dication form are 446 and 664 nm for $TPPH_2$, 451 and 674 nm for $TP(OH)(H)_3PH_2$, 456 and 703 nm for $TP(OH)PH_2$, 450 and 674 nm for $TP(Bu^t)PH_2$, 453 and 683 nm for $TP(OH)(Bu^t)_3PH_2$, 456 and 694 nm for $TP(OC)PH_2$, 456 and 697 nm for $TP(OH)(OC)_3PH_2$, respectively . The ratio of the absorbance of the Q(0–0)/Soret band for the dication form is 0.13 for $TPPH_2$, 0.20 for $TP(OH)(H)_3PH_2$, 0.22 for $TP(OH)PH_2$, 0.15 for $TP(Bu^t)PH_2$, 0.21 for $TP(OH)(Bu^t)_3PH_2$, 0.20 for $TP(OC)PH_2$, 0.21 for $TP(OH)(OC)_3PH_2$. The absorbance ratio for the mono *p*-OH substituted tetraphenylporphines for the dication form is higher than that for the porphines without a *p*-OH group.[10]

Fig. 6 shows the spectral changes of the $TP(OH)(H)_3PH_2$–EC composite films without DOP. The introduction of one *p*-OH group resulted in red shifts of both the Soret- and Q-bands. Moreover, λ_{max} of Q(0–0) band of the dication form was shorter than that of the dication form of tetrakis(*p*-hydroxyphenyl)porphine. In ambient HCl, λ_{max} values of Soret- and Q(0–0)-bands were 454 and 677 nm for $TP(OH)(Bu^t)_3PH_2$, and 456 and 693 nm for $TP(OH)(OC)_3PH_2$, respectively. For the mono *p*-OH substituted tetraphenylporphines, the sensitivity to HCl gas of the Soret- and Q(0–0)-band was considerably higher than that of the unsubstituted tetraphenylporphine. It is confirmed that for the EC composite films replacing the *para*-hydrogen in the phenyl group with a hydroxy group would also be effective in enhancing the absorbance of the Q(0–0) band of the dication form with red shifts, in which the degree of the red shifts increases with the number of *p*-OH groups.

The calibration curves at the Soret- and Q(0–0)-bands are shown in Fig. 7 and 8, respectively, for the composite films without DOP. The sensitivity at both bands was in the following order: $TPPH_2 < TP(OH)(Bu^t)_3PH_2 < TP(OH)(OC)_3PH_2 \leqslant TP(OH)(H)_3PH_2$. This trend can be ascribed to the electron donating power of the *para* substituents. The ratio of $\log(I_0/I)$ at the Q(0–0) band and $\log(I_0/I)$ at the Soret band upon exposure to 12.7 ppm HCl was evaluated to be 0.88, 0.85, 0.69, 0.68, 0.40 and 0.35 for $TP(OH)(OC)_3PH_2$, $TP(OH)(H)_3PH_2$, $TP(OH)(Bu^t)_3PH_2$, $TP(OC)PH_2$, $TPPH_2$ and $TP(Bu^t)PH_2$, respectively. The introduction of one *p*-OH resulted in the enhancement of the HCl sensitivity at the Q(0–0)-band. It is interesting to note that at the Q(0–0) band, the sensitivity of the composite films with tetraphenylporphine substituted with a single *p*-OH group was higher than that of $TPPH_2$-composite films doped with DOP (as mentioned the HCl sensitivity of $TPPH_2$ composite film was enhanced by the addition of DOP).

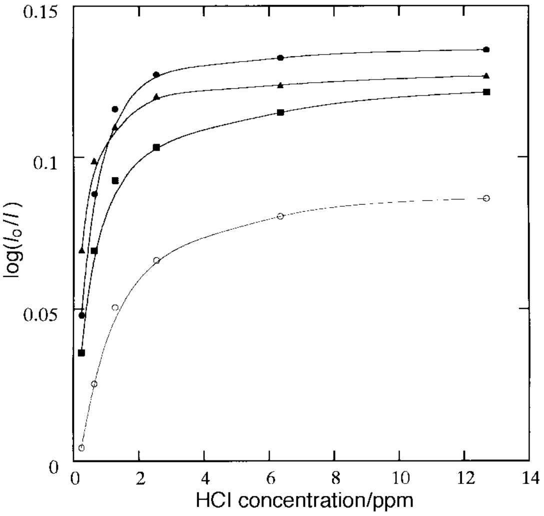


Fig. 7 HCl concentration dependence of $\log(I_0/I)$ at the Soret band at 30 °C. Porphine concentration: 5×10^{-5} mol per g EC; (○) $TPPH_2$, (●) $TP(OH)(H)_3PH_2$, (■) $TP(OH)(Bu^t)_3PH_2$, (▲) $TP(OH)(OC)_3PH_2$.

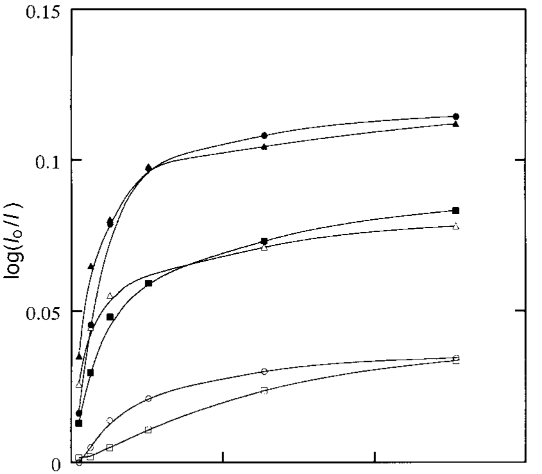


Fig. 8 HCl concentration dependence of $\log(I_0/I)$ at the Q(I)-band at 30 °C; (○) $TPPH_2$, (●) $TP(OH)(H)_3PH_2$, (□) $TP(Bu^t)PH_2$, (■) $TP(OH)(Bu^t)_3PH_2$, (△) $TP(OC)PH_2$, (▲) $TP(OH)(OC)_3PH_2$.

The response behavior of $TP(OH)(OC)_3PH_2$ is shown in Fig. 9. While both response and recovery times of mono *p*-OH substituted tetraphenylporphines are considerably longer than that of tetraphenylporphine, the response behavior was reversible and became faster with increasing temperature. The response and recovery times of 5-(*p*-hydroxyphenyl)-10,15,20-triphenylporphine composite were faster than those of the 5,10,15,20-tetrakis(*p*-hydroxyphenyl)porphyrin composite. When the working temperature was increased from 45 to 60 °C, the percent reflectance of the Soret-band at 12 ppm HCl changed from 86 to 94 for $TPPH_2$ and remained the same (78) for $TP(OH)(OC)_3PH_2$. The introduction of a single *p*-OH group resulted in a decrease in the temperature coefficient of the sensitivity for both the Soret- and Q(0–0)-bands, as shown in Fig. 9. Significant deterioration of the sensitivity under irradiation with filtered light (> 600 nm) was not observed for more than 50 d for the 5-(*p*-hydroxyphenyl)-10,15,20-tris(*p*-R-substituted-phenyl)porphine composite films without DOP.

Furthermore, tests in other gaseous environments showed that the Soret- and Q-bands of the films were also sensitive to vapors from aqueous solution of HNO_3, HF or HCOOH, while for a benzene solution, the Soret and Q-bands were insensitive to HCOOH which may be related to the water content. Furthermore, they were mostly insensitive to vapors from CH_3COOH or C_2H_5COOH. To clarify the reasons for these observed differences in the sensitivity (selectivity), we needed to measure the sorption characteristics of the composite films, since the sensitivity is influenced by the sorption ability and solubility of the composite film for these organic acids and water. In dry conditions, the sensitivity to HCl gas was not influenced by the coexistence of 2000 ppm of H_2 and CO_2. The percent reflectance at the Soret band ($\lambda_{max} = 440$ nm) decreased by only 1% for 8 ppm NO_2 and 0.5% or less for 10 ppm NO. The changes for NO_x may be attributed to the formation of HNO_3 by the reaction with water as a contaminant. It is expected that the sorption of NO_2 results in the formation of a radical π-cation or π-dication; the π-cations are very unstable in solution, being oxidized to π-dications as reported by Carnieri and Harriman.[11] The π-dications are also reactive and react to give the acid dication by protonation. The lack of observation of spectral changes indicating the formation of radical π-cation or π-dication may be related to the difference in permeability of the EC composite for HNO_3 and NO_x and/or the difference in stability of acid dications and radical cations in the EC matrix. The percent reflectance at the Soret band decreased by only 0.5% for 1 ppm Cl_2 while

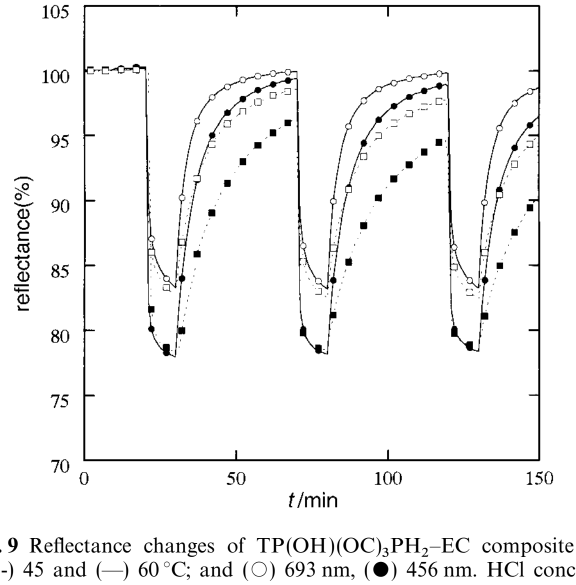


Fig. 9 Reflectance changes of $TP(OH)(OC)_3PH_2$–EC composite at (----) 45 and (—) 60 °C; and (○) 693 nm, (●) 456 nm. HCl concentration is changed from 0 ppm (nitrogen) to 12.7 ppm and the reflectance measured again.

the presence of a large excess of Cl_2 (5 ppm) resulted in a decrease of 10% and only partial recovery was observed when the introduction of Cl_2 gas was stopped. It is well known that Cl_2 interacts with water and forms HCl and HClO. HClO is an unstable compound and decomposes to HCl and O_2, especially under light irradiation. If Cl_2 is changed completely to HCl, a reversible response behavior is expected. A lack of reversibility to Cl_2 may be due to some other side reactions with the porphine, such as chlorination. In any case, a more detailed discussion about cross-sensitivity requires other results.

Conclusions

Spectral changes of tetraphenylporphine and its derivatives dispersed in ethylcellulose were examined for detection of sub-ppm levels of HCl gas. The sensitivity in the Q(0–0) band region is enhanced by replacing the hydrogen *para* to the phenyl group with electron donating substituents, while the response time is prolonged. Marked deterioration of the sensitivity under irradiation with filtered light (> 600 nm) was not observed for more than 50 days, for the composite films examined. An HCl gas sensor based on mono-substituted tetraphenylporphine with a *p*-OH in one phenyl group shows superior performance for detection of emissions of ppm levels of HCl gas, 5 ppm being the environmental standard for HCl gas.

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