Chapter 7

Gas Sensing Applications of Porphyrins
7.1. Hydrogen chloride gas sensor based on porphyrin coated glass plate

Optochemical sensing of small molecules has received much attention in recent years due to its versatility and easy recognition [1-3]. Since hydrogen chloride (HCl) is the source for acid rain as well as a work place hazard with a short term exposure limit of 5 ppm, sensing and standardization of its level in the atmosphere are very important. The concentration of HCl in the environment is now strictly regulated in many countries owing to its hazardous nature. To monitor the emission of HCl from industries into the environment, an efficient sensor has to be developed. Extensive studies have been carried out to utilize porphyrin and its derivatives for the fabrication of sensors to detect acid gases [4-17]. Porphyrin and its derivatives are very stable in nature and have absorption characteristics in the region of 350 to 750 nm [18,19]. The appearance of strong Soret and Q bands of porphyrins in the visible region enables the researchers to think about the use of these dyes for the fabrication of optochemical sensors. The reported sensors are mainly based on the incorporation of porphyrin dyes into hydrophobic membrane, polymer composites materials, sol-gel etc. [3-10,15-17]. In the case of polymeric composite materials based sensors, the sensing ability of the sensor depends on the glass transition temperature of the polymeric materials [7]. Extensive studies have been carried out on porphyrin derivatives based HCl gas sensors [3,4-10,15-17]. In this chapter, the HCl gas sensing properties of meso-tetramesitylporphyrin (MTMP), meso-tetraphenylporphyrin (MTPP) and meso-tetrakis-(4-nitrophenyl)porphyrin (MTNP) adsorbed on glass plate are studied.
7.2. Optochemical sensing of HCl gas using meso-tetramesitylporphyrin deposited glass plate

Exposure of the solid state sensor to HCl vapor leads to the protonation of meso-tetramesitylporphyrin (PMTMP) as shown in Figure 7.1.

![Diagram of protonation and deprotonation of MTMP molecule]

\[ \text{MTMP} \xrightarrow{+ 2H^+} \text{PMTMP} \xleftarrow{-2H^+} \]

**Figure 7.1.** Protonation and deprotonation of MTMP molecule.

To understand the nature of the protonation of MTMP by HCl, the protonation of MTMP in dichloromethane-methanol mixture was studied by UV-vis and fluorescence spectral techniques. The changes in the Soret band (452 nm) absorbance were used to estimate the amount of HCl present in gaseous phase.
7.2.1. UV-Vis and fluorescence spectral studies of MTMP protonation

UV-vis spectra of MTMP in dichloromethane-methanol mixture in the presence of different concentrations of HCl are shown in Figures 7.2 and 7.3. To facilitate the protonation of MTMP by HCl, we have used dichloromethane-methanol mixture. The characteristic Soret or B band at 418 nm (Figure 7.2 (curve i))

![Graph showing UV-Vis spectra](image)

**Figure 7.2.** Absorption spectra of 1 mM MTMP in dichloromethane-methanol mixture after the addition of (i) 0, (ii) 0.2, (iii) 0.6, (iv) 1.0, (v) 1.6, (vi) 1.8, and (vii) 2 mM of HCl and (viii) addition of excess triethylamine to (vii).
and Q bands at 514, 547, 590 and 647 nm (Figure 7.3 (curve i)) were observed for MTMP with usual relative intensities [20]. Among the Q bands, the $Q_{x}(0-0)$ band at 514 nm is the most intense and the $Q_{z}(0-0)$ band at 647 nm is the least intense for MTMP. It is known that the Soret and Q bands of porphyrins were highly sensitive to the protonation [21,22]. Addition of HCl to the solution of

![Absorption spectra](image)

**Figure 7.3.** Absorption spectra in the Q-band region of MTMP in dichloromethane-methanol mixture after the addition of (i) 0, (ii) 0.6, (iii) 1.0, (iv) 1.6, and (v) 2 mM HCl.

MTMP in dichloromethane-methanol mixture leads to a protonation of tertiary nitrogen atoms resulting changes in the absorbance (Figures 7.2 and 7.3) and the
color of the solution from reddish pink to fluorescent green (Figure 7.4). After protonation of MTMP, the Q_s(0-0) band at 647 nm became the most intense with a 22 nm blue shift (Figure 7.3 (curve v)) and the Q_y(0-0) band at 514 nm became the least intense band. The band Q_s(0-0) at 647 nm is attributed to the formation of dication [21]. The Soret band of porphyrin is conserved with a 14 nm (418 to 432 nm) red shift (Figure 7.2) due to the protonation of MTMP. The appearance of isosbestic point at 425 nm in Figure 7.2 clearly confirmed the conversion of MTMP to PMTMP. Addition of triethylamine (TEA) to the solution of PMTMP revert the spectral characteristics of MTMP owing to the deprotonation of PMTMP to MTMP by TEA (Figure 7.2 curve viii).

![MTMP PMTMAP](image)

**Figure 7.4.** Meso-tetramesitylporphyrin in dichloromethane-methanol mixture in the absence (MTMP) and presence (PMTMP) of HCl.

The emission spectra obtained for the titration of MTMP in dichloromethane-methanol mixture against aqueous HCl are shown in Figure 7.5.
The excitation of MTMP at 418 nm results in a strong emission band at 650 nm along with an additional shoulder emission band at 714 nm corresponding to the $Q_x(0-0)$ and $Q_x(0-1)$ bands, respectively [21]. It is well known that the

\begin{figure}
\centering
\includegraphics[width=\textwidth]{emission_spectra.png}
\caption{Emission spectra of MTMP in dichloromethane-methanol mixture (excitation wavelength = 418 nm) containing (i) 0, (ii) 0.2, (iii) 0.6, (iv) 1, (v) 1.4, (vi) 1.6, and (vii) 2 mM of HCl and (viii) addition of excess triethylamine to (vii).}
\end{figure}

fluorescence intensity of porphyrin depends upon the concentration of acid present in the solution [21]. When the concentration of HCl increased in the solution of MTMP, the emission intensities of both peaks at 650 and 714 nm were decreased and a new broad emission band appeared between 550 and 600 nm (Figure 7.5).
The decrease of emission intensities is due to the quenching behavior of HCl. The observed broad emission band between 550 and 600 nm (Figure 7.5) is responsible for the fluorescent green color of PMTMP (Figure 7.4). The emission intensity at 650 nm was reverted back to its original form following the addition of excess TEA to the solution (Figure 7.5, curve viii) with the color of the solution was changed from fluorescent green to reddish pink.

**Figure 7.6.** Optimized structures of MTMP and PMTMP.

*ab-initio* calculations were carried out to visualize the effect of protonation on the stability and structural changes of MTMP. Initially MTMP has a planar structure (Figure 7.6) and all mesityl groups are perpendicular to the plane of the porphyrin ring. Upon protonation of the tertiary nitrogen atoms of the porphyrin core, the planarity was destroyed and thus a structural change from a planar to saddle conformation was predicted. The observed 14 nm red shift in the Soret region of the protonated MTMP (Figure 7.2) is mainly due to the loss of the
planarity of the porphyrin ring thereby increasing conjugation with the mesityl
groups in solution.

7.2.2. Characterization of solid state sensor

The solid state sensor (thin film of MTMP on glass plate) was characterized
by UV-vis absorption spectroscopy. Figure 7.7 shows the UV-vis spectrum
obtained for MTMP deposited glass plate. It shows a more intense absorbance for
Soret band at 434 nm along with less intense peaks at 520, 546, 595, and 650 nm

![Absorption spectrum](image)

**Figure 7.7.** Absorption spectrum of MTMP deposited on a glass plate. Inset:
Absorption spectrum of MTMP in dichloromethane.

corresponding to Q bands (Figure 7.7). The observed characteristic spectral bands
of MTMP deposited glass plate clearly indicate that MTMP was adsorbed on the
glass plate. In contrast to MTMP in dichloromethane (Figure 7.7 inset), a 16 nm
red shift was observed for MTMP deposited glass plate. This may be attributed to
the aggregation of the porphyrin molecules in solid state [23]. Further, the aggregation of porphyrin molecules upon protonation was confirmed by SEM images. Figure 7.8, curve b shows the discrete aggregate formation when MTMP film (Figure 7.8, curve a) was exposed to HCl gas. Rearranged Beer-Lambert equation was used to calculate the surface density \(d_{\text{surf}}\) of the porphyrin molecules [24].

\[
d_{\text{surf}} = A \times \varepsilon^{-1}
\]  

(7.1)

where \(A\) is the Soret band absorbance of MTMP and \(\varepsilon\) is molar extinction coefficient. The surface density of MTMP molecules in MTMP film was found to be \(6.7 \times 10^{-7} \text{ mol cm}^{-2}\).

Figure 7.8. SEM images of (a) MTMP film on glass plate and (b) MTMP film exposed to HCl gas.
7.2.3. Detection of HCl gas

To obtain quantitative information about the sensing properties of solid state sensor, UV-vis spectra were recorded and the corresponding responses for successive exposure of HCl vapor to solid state sensor are shown in Figure 7.9. As the exposure time of HCl increases, the absorbance of Soret band at 452 nm

![Graph showing absorbance vs wavelength for MTMP deposited glass plate before and after exposure to HCl vapor.]

**Figure 7.9.** Absorption spectra of MTMP deposited glass plate before (a) and after (b) 5, (c) 120, and (d) 180 s exposure to 0.4 ppm HCl vapor.

increases significantly in addition to other bands. The absorbance changes of Soret band at 452 nm were monitored with respect to the concentration of exposed HCl gas. As shown in Figure 7.10, the solid state sensor shows a sharp increase in the
absorbance after exposed to 0.4 ppm HCl gas which implies the sensing capability of solid state sensor towards HCl gas.

![Graph showing absorbance over time with different concentrations of HCl]

**Figure 7.10.** Absorption spectra of MTMP deposited glass plate before (a) and after (b) 5, (c) 120, and (d) 180 s exposure to 0.4 ppm HCl vapor.

Exposure of the sensor to HCl gas leads to the conversion of MTMP into PMTMP and thus the intensity of Soret band at 452 nm sharply increases (Figure 7.10). When an inert gas (N₂) was passed after reaching the equilibrium state, the Soret band intensity at 452 nm started to decrease and attained the original intensity as observed for MTMP suggesting that PMTMP was reverted to MTMP. A set of four successive HCl exposures to solid state sensor was carried out in the
range of 0.4-0.1 ppm (Figure 7.10). The sensor showed good response to even at the concentration of 0.1 ppm HCl gas with good reversibility. Absorbance variation ($\Delta A$) was obtained from the differences between the absorbance intensities of the MTMP thin film at 452 nm before and after exposure to different HCl concentrations [21]. To obtain the calibration curve, we have plotted the concentrations of HCl against the ($\Delta A$). As the concentration of HCl gas increases, the absorbance of the Soret band also increases yielding the following equation

$$Absorbance = 0.1692(\pm0.0118) \times concentration + 0.06135(\pm0.0032)$$ \hspace{1cm} (7.2)

(Number of data = 4 ; correlation coefficient =0.9959). The complete reversibility of 0.4 ppm HCl gas exposed sensor was attained after passing N$_2$ for 16 min, which indicates that the sensor is fully reversible but the rate of reversal is markedly slower than the rate of the response. The detection limit of the solid state sensor found to be 0.03 ppm. The detection limit was measured by analyzing standards that are zero in concentration then measuring the standard deviation of the measurements. In order to reduce the probability of a false non-detection, the standard deviation is then multiplied by the factor 3.0 [25].

7.2.4. Stability and reversibility of the solid state sensor

The reversibility and sensing trend of solid state sensor in humid condition were established from the visible spectral studies. The reversibility of the sensor
was checked by exposing it to 0.4 ppm HCl gas consecutively for three times with different amounts of humidity (Figure 7.11). The reversibility of the sensor is

![Graph showing absorbance over time with labeled steps: a, N2, b, HCl, H2O, c.](image)

**Figure 7.11.** Reversibility and recovery of solid state sensor to 0.4 ppm of HCl with (a) 0 %, (b) 25 % and (3) 75 % of humidity.

slightly affected by the humidity. As the amount of water vapour increases the absorption intensity at Soret band (452 nm) decreases and reaches steady state from second increment of water vapour (Figure 7.11). Moreover, the recovery rate is high while compared to the use of HCl in dry nitrogen gas (Figure 7.10) as evidently seen from Figure 7.11. The stability of the solid state sensor was also checked by exposing it into open atmosphere. The solid state sensor was highly stable for several months. The present solid state sensor has several advantages.
over the reported solid state sensors based on porphyrin derivatives [3,4-10,15]: (i) the fabrication of the present sensor is very simple and highly stable against humid conditions and (ii) the sensing property is not much affected by humidity due to the hydrophobic nature of the MTMP porphyrin film.

7.3. Optochemical sensing of HCl gas using MTPP deposited glass plate

The HCl sensing properties of MTPP film was studied similar to MTMP. The MTPP was coated on a glass plate and used for HCl sensing. The protonation of MTPP (Figure 7.12) leads to 23 nm red shift of Soret band. The deprotonation

![Absorption Spectra](image)

**Figure 7.12.** Absorption spectra of MTPP deposited glass plate (a) before and (b) after 180 s exposure to 0.4 ppm HCl vapor. The same film after flushing with nitrogen gas for (c) 1200 s and (d) 3200 s.
of the porphyrin was checked with flushing of N₂ gas and found that the reversibility of MTPP is very poor (Figure 7.12). The reversibility was not observed even after 1 hr of flushing out with N₂ gas (Figure 7.13). The absorption changes of MTPP coated glass plate towards the HCl gas is shown in Figure 7.13. After the introduction of HCl gas, the absorption at 458 nm sharply increased. After reaching the steady state, the HCl gas was cut off and the N₂ flush out was introduced. The decrease in absorption was not sharp and regular. The

![Absorption graph (Figure 7.13)](image)

**Figure 7.13.** Absorption changes at 458 nm of MTPP deposited glass plate exposed to 0.4 ppm HCl vapor.
complete reversibility was not achieved even after 45 min. This indicated that the MTPP coated film can not be used as HCl sensor. The poor reversibility of the sensor may be due to the absence of bulky group like mesityl at meso positions.

7.4. Optochemical sensing of HCl gas using MTNP deposited glass plate

Similar to MTPP, MTNP film was also screened for the HCl sensing properties. The MTNP was coated on a glass plate and used for HCl sensing. The protonation of MTNP (Figure 7.14) leads to 23 nm red shift of Soret band. The

![Absorption spectra of MTNP deposited glass plate](image)

**Figure 7.14.** Absorption spectra of MTNP deposited glass plate before (a) and after (b) 180 s exposure to 0.4 ppm HCl vapor. The same film after flushing with nitrogen gas for (c) 1200 and (d) 3200 s.
protonation of MTNP by HCl gas was not resulted in a significant change in the absorption of the Q band at 670 nm as in the case of MTMP or MTPP (Figure 7.14). The absorption changes of MTNP coated glass plate towards HCl gas is shown in Figure 7.15. After the introduction of HCl gas, the absorption at 461 nm sharply increased. After reaching the steady state, the HCl gas was cut off and the N₂ gas flush out was introduced. The decrease in absorption was not sharp and complete reversibility was not observed even after 45 min.

![Absorbance over time graph](image)

**Figure 7.15.** Absorption changes at 461 nm of MTNP deposited glass plate exposed to 0.4 ppm HCl vapor.
The observed results indicated that MTNP coated glass plate can not be used HCl sensing due to the poor reproducibility. The poor reversibility of the MTNP coated glass plate may be due to the flexibility of porphyrin ring in the absence of bulky group like mesityl at meso positions.

7.5. Conclusion

In the present chapter, we have adopted a very simple procedure to fabricate the solid state sensor by coating meso-substituted porphyrin derivatives on glass plate (solid state sensor) and examined optochemical sensing of HCl gas. The protonation and deprotonation of MTMP in solution were followed by absorption and fluorescence spectral techniques. Protonation of MTMP by HCl is the cause for the color change from reddish pink to fluorescent green and also a broad emission band observed between 550 and 600 nm. The solid state sensor proposed in this paper has several advantages including ease in preparation and high stability against humid conditions. The lowest detection limit of 0.03 ppm HCl was obtained for the present solid state sensor. On the other hand, the other porphyrin derivatives, MTPP and MTNP coated glass plates were not suitable for HCl gas sensing due to their irreversible nature towards protonation and deprotonation.
7.6. References


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