The MPc materials such as CuPc, nickel phthalocyanine (NiPc), cobalt phthalocyanine (CoPc), zinc phthalocyanine (ZnPc) and iron phthalocyanine (FePc) used in this work were synthesized in our laboratory using phthalic anhydride urea method. Synthesised materials were characterized with different techniques such as X-ray diffraction (XRD), UV-Visible absorption (UV-Visible) spectra, Fourier Transform Infrared (FTIR) spectra, Thermo Gravimetric Analysis/Differential Thermal analysis (TGA/DTA). The samples were prepared in the form of pellets and films. Films were prepared using spin coating technique on glass substrate. The spin coated CuPc films were characterized using XRD, UV-Visible spectra, FTIR, Scanning Electron Microscopy (SEM) and Energy Dispersive Spectra (EDS). The response of pellet samples and spin coated films were studied for NO$_2$ gas sensing. In order to study gas sensing performance the experimental setup was developed in laboratory. Prepared samples were tested for the pollutant gas NO$_2$ and water vapor. Taking into consideration the application area and operating power consumption of samples, I operated and tested samples at ambient temperature. Prototype device was constructed for humidity sensing.

The $\lambda_{\text{max}}$ values and energy band gap values were calculated using standard protocol from UV-Visible spectra of the CuPc, CoPc, NiPc, ZnPc and FePc. The IR spectra analysis showed that the region between 400 cm$^{-1}$ to 1350 cm$^{-1}$ is same for all MPcs which is the region of MPc skeleton. Region between 1350 cm$^{-1}$ and 1550 cm$^{-1}$ is different for different MPc which depends on the metal atom present in the MPc molecule and the peaks between 1700 cm$^{-1}$ and 2000 cm$^{-1}$ are weak and are due to aromatic ring which are again same for all MPcs.

All the materials showed response in terms of change in resistance after the exposure of samples to NO$_2$ gas. Initial resistance that is the resistance of sample in air ($R_a$) of all the samples was high of the order of Mega ohm ($10^6$ ohm) or Giga ohm ($10^9$ Ohm) and after exposure to NO$_2$ it decreases to KOhm. It was observed
that the sensitivity decreases with increasing NO\textsubscript{2} gas concentration in the surrounding air of the samples. NiPc showed the maximum sensitivity (99\%) and ZnPc showed the minimum sensitivity (55\%) to 0.5 volume\% concentration of NO\textsubscript{2} gas with the samples prepared in the form of pellets. It was found for all the studied MPc pellets that the response time decreases with increasing gas concentration. NiPc showed lowest response time of 1.85 minute, CuPc, CoPc and ZnPc showed moderate and FePc showed highest response time that is 100 minute for a 0.5 volume\% concentration of NO\textsubscript{2} gas. As far as the sensitivity is considered, CuPc, CoPc and NiPc are suitable materials than ZnPc and FePc for NO\textsubscript{2} sensing. But if the response time is taken into consideration only NiPc CoPc and CuPc are suitable materials. If response time and sensitivity both the parameters are simultaneously considered then NiPc was found to be the best choice. Average recovery ratio of the samples exposed to 0.5 volume\% concentration of NO\textsubscript{2} gas is 0.06. The recovery ratio of CuPc is 0.14 which is the highest value as compared with that of other studied materials. Also the CuPc showed low recovery time (23.5 minute) as compared same with other materials. Above mentioned values of different parameters shows that the NiPc and CuPc materials are suitable materials to use them as NO\textsubscript{2} gas sensing material. Low recovery in ambient conditions and low cost of the materials and simple preparation of samples in the form of pellets suggest that these sensors can be used for single use applications.

The increasing value of the rate constant in the gas exposing stage of MPc pellets with increasing NO\textsubscript{2} gas concentration revealed that the rate of change of instantaneous sensitivity increases with increasing gas concentration. The dependence of the rate of change of sensitivity on the gas concentration was used to detect and determine the unknown gas concentration in the surrounding air of the sample. The rate was determined within the few seconds as soon as the sensor was exposed to nitrogen dioxide.

CuPc films were prepared using spin coating technique on the glass substrate with optimized parameters. The average thickness of the films thus prepared was 200 nm. Current-Voltage (I-V) characteristics result indicated that
the pristine films show more current than the annealed films. The reason behind the increase of resistance of annealed films may be the crystallization of film material, modification in the film morphology or may be the change in grain size and grain boundaries. The doping of MPcs due to fluorine from TFAA may be one of the reasons of change in resistance of films before and after the annealing. Energy gap estimated from the Ultraviolet-Visible spectra are 1.6 eV for pristine film and 1.7 eV for annealed film. The stability in the peak positions in the absorbing region of absorption spectra of pristine and annealed films show the stability of the structure of CuPc. The crystal parameter marker bands are observed at 718 cm$^{-1}$, 754 cm$^{-1}$ and 769 cm$^{-1}$ in the IR spectra of CuPc spin coated films. This confirms that $\alpha$- crystalline form is predominantly present in the prepared films with a very small percentage of the $\beta$-form. The value of interplanner distance $d$ determined from X-ray spectra of annealed films = 12.87 Å which indicates that the crystal structure of CuPc films is $\alpha$ phase. The grain sizes of the CuPc films annealed with temperatures from 100°C to 300°C were determined from the X-ray diffraction data indicates that the grain size increases initially from temperature 100°C to 200°C and then decreases at 250°C and 300°C. Initial increase of grain size may be due to increasing crystallization as a result of annealing. The reduction in grain size from 200°C temperature annealed film to 250°C temperature annealed film can either be due to partial sublimation, recrystallisation or phase transformation from $\alpha$ to $\beta$. If reduction in grain size is due to the phase transformation then it can be concluded that the phase transformation of CuPc occurs at and above 250°C. The films prepared by the spin coating method, the $\alpha$ phase crystallites undergo a complete transformation into $\beta$ phase after post annealing at temperatures higher than 250°C.

The resistance of CuPc spin coated film annealed at 150°C temperature was 1100 MΩ. The response of CuPc spin coated annealed (150°C) film in terms of change in resistance of the film after exposure to NO$_2$ gas show that the resistance of the film decrease from 1100 MΩ to 50 MΩ. The sensitivity of CuPc spin coated films annealed with temperatures 50°C to 300°C to 500 ppm NO$_2$ increases as the annealing temperature increases from 50°C to 150°C and then the sensitivity decreases as the temperature increases from 150°C to 300°C. This might be due to
the presence of mixed α and β morphology of CuPc present in the initial stage with high percentage of α and low percentage of β morphology which already studied in FTIR and UV visible studies, but in the latter stage, films annealed with higher temperature than 200°C, there might be the large conversions from α to β morphology. In the high temperature annealed films population of β phase may be large and hence there is decrease of sensitivity at higher annealing temperature. The decrease in response time of the films was observed, as the annealing temperature was increased from pristine film to 150°C and again increase was observed in response time as the annealing temperature was increased from 150°C to 300°C. Increase of grain size with annealing temperature corresponds to the decrease in active surface area. Decrease in active surface area leads to less interactions per second and hence increases the response time. The sensitivity decreases greatly due to the formation of gross-crystalline structure as a result of heat treatment. As phase transformation occurs from α to β above 200°C annealing temperature and the β polymorph is more compact than the α polymorph, hence may be showing low sensitivity and high response time at higher annealing temperature of the films. If the highest value of sensitivity (98 %) and lowest response time (120 seconds) is considered then the films annealed with temperature 150°C are suitable for NO₂ sensing applications. The films annealed for 2 hours duration (annealing temperature = 150°C) has highest sensitivity and are faster and the films annealed for longer times such as 3, 4 and 5 hours are low sensitive to the nitrogen dioxide and also they are slower. Increase of the degree of crystallization with increasing annealing time may be the reason. Also, this may be due to the fine-grain crystallites present in the pristine films were may transformed to a structure with grosser grains as a result of coalescence and reorganization of the grains during the heat treatment. The grains become larger when the annealing time is increased. The annealed films have a gross-crystalline structure and hence the exposing area of the film surface decreases. This causes the slow decrease of film resistance during the gas sensing period. This causes the the high response time of the heat treated films more than 2 hours. It is also seen that the sensitivity decreases after annealing. The sensitivity is related to the surface area and adsorption site to NO₂ gas. The crystal size of CuPc film becomes larger after
annealing. This causes smaller surface area which may result in smaller sensitivity. Comparatively, the gas sensitivity decreases little with increasing annealing time because there may be no significant change in crystal size. Annealing at lower and higher temperature than 150 °C and short and long time annealing than 2 hours slows down the response rate. The CuPc spin coated films annealed with temperature 150°C for 2 hours duration are suitable for NO₂ sensing applications as they show highest sensitivity (98 %) and lowest response time (120 second). The recovery ratio increases as the annealing temperature of the films increases. This may be due to the decrease of surface area of annealed films. As the annealing temperature increases, the phase transformation from α phase to β phase may takes place. The β phase is more compact than α phase morphology of the CuPc films. Hence the compactness of the CuPc crystals in the film also increases. This may cause less diffusion of NO₂ molecules in the bulk of the film and hence may be the improvement in the recovery ratio at longer time annealing of the films. The CuPc spin coated annealed film shows increase in sensitivity with increase in concentration to the response towards NO₂. The sensitivity increases up to 200 ppm NO₂ gas concentration. Sensitivity for higher concentration than 200 ppm is almost constant. Significant decrease in response time was observed as the gas concentration was increased from 50 ppm NO₂ concentration to 500 ppm NO₂ concentration. The steady response time is seen from 400 ppm gas concentration.

In situ FTIR experiment of CuPc spin coated film with and without NO₂ doping showed that in C-C stretching (1250 cm⁻¹ -1700 cm⁻¹) region the peak at 1420 cm⁻¹ completely disappears under the influence of NO₂. The intensity of C-H in-plane bending (1000 cm⁻¹ – 1200 cm⁻¹) and C-N stretching (1050 cm⁻¹ – 1650 cm⁻¹) decreases with NO₂ doping. In the IR spectra of CuPc films with NO₂ doping, a new peak is appeared at 1458 cm⁻¹. It is may be due to Cu-O-NO. IR spectra of CuPc spin coated films with and without NO₂ doping showed evidence for the interaction on NO₂ molecules with the CuPc molecules.