

Conducting Polymers Functionalized with Phthalocyanine as Nitrogen Dioxide Sensors

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Abstract: The conducting polymers such as polyaniline, polypyrrole and polythiophene were functionalized with copper phthalocyanine using chemical oxidation method. The obtained polymers viz. PANI-CuPc, PPy-CuPc and PT-CuPc were studied as chemical sensors by their response characteristics after exposure to various chemical vapors such as methanol, ammonia and nitrogen dioxide. The results obtained showed that these polymers have moderate sensitivity towards the methanol as well as ammonia vapors whereas they show tremendous sensitivity towards nitrogen dioxide vapors. The sensitivity factor of as high as 50,000 was obtained for PT-CuPc polymers in nitrogen dioxide. In comparison to this, the sensitivity factors of about 100 and 40 were obtained, when these polymers were exposed to ammonia and methanol vapors. The very high selectivity towards the nitrogen dioxide was explained on the basis of charge transfer complex formed between, the phthalocyanine donor and nitrogen dioxide acceptor molecules. On the other hand, ammonia becomes a competing electron donor in CuPc containing conducting polymers. The very low response towards the methanol may be explained on the basis very little charge transfer / interaction between CuPc containing polymers and methanol. Thus, CuPc incorporated conducting polymers have much higher selectivity than their original homopolymer

Key words: Phthalocyanine, Nitrogen dioxide sensors

Introduction

The importance of environmental gas monitoring is well understood and much research has focused on the development of suitable gas-sensitive materials. Recently, there has been considerable interest in exploiting organic substances such as porphyrin [1], phthalocyanines [2,3] and doped conductive

polymers [4]. The conducting polymers are good candidates for the elaboration of chemical or electrochemical sensors in two main ways. (1) As sensitive components: The electronic conductivity related to the redox state (doping level) of a conducting polymer is modulated by the interaction with various substrates. Changes in parameter values, such as resistance, current or electrochemical potential, give a straightforward sensor response of the studied phenomena. (2) As a matrix for specific immobilisation: Conducting polymers are often infusible and insoluble. Consequently, immobilisation by entrapment of specific molecules that are capable of substrate recognition can be carried out mainly during polymerisation process. However, this growing reaction added to the entrance of negatively charge species (sometimes positive ones) makes it possible to entrap various moieties easily in a one-step process, with the further advantages of intrinsic porosity and electronic accessibility.

In its simplest form, a sensor consists of a planar inter-digital electrode coated with a conducting polymer thin film. If a particular vapour is absorbed by the film and affects the conductivity, its presence may be detected as a conductivity change. The first evaluation of conducting polymer as sensitive components in chemical sensors are based on their redox interaction with some gases, including a variation of the doping level, resulting in a quite straight forward conductance, monitoring of gas sensor response over orders of magnitude [5]. Inter-digited electrodes covered by a PPy layer have been tested by Miasik et.al.[6] for the detection of NH_3 , NO_2 and H_2S gases. Yoneyama et.al.⁷ have shown that the electropolymerized PPy films exhibit noticeable gas sensitivities to electron acceptor gases such as PCl_3 , SO_2 and NO_2 at room temperature; especially when PPy is reduced electrochemically before exposure. The same group also investigated the gas sensing properties of polythiophene film⁸, but they found a more irreversible behaviour in the conductivity change after exposure to NH_3 and H_2S .

The observation that the semi-conducting properties of phthalocyanine are modulated by the absorption and de-sorption of gases has led to significant efforts toward their incorporation in chemical sensors. The phthalocyanine sensors have been reported by early workers⁹. These workers had reported that NO_2 to have large effects (6-8 orders of magnitude) on conductivity of a variety of sublimed phthalocyanine films. It is hoped that making appropriate substitutions of metals in the cavity and organic substituents at the periphery of the phthalocyanine structure may develop the gas specificity.

In our laboratory, extensive studies were carried out on the direct incorporation of phthalocyanine into conducting polyaniline, polypyrrole and polythiophene using chemical as well as electrochemical oxidation methods. In the present paper we are only dealing with the chemical sensitivity studies of conducting polymers functionalized with copper phthalocyanine namely, polyaniline (PANI-CuPc), polypyrrole (PPy-CuPc) and polythiophene (PT-CuPc). These polymers were tested towards the chemical vapours of nitrogen dioxide, ammonia and alcohol.

Experimental

Synthesis of Polymers

General method of syntheses of these conducting polymers involves the chemical oxidation reaction of monomer aniline, pyrrole or thiophene. The solvent used for synthesis of polyaniline and

polypyrrole was mixture of NMP: H₂O (1:1). The nitrobenzene was used in the preparation of polythiophene. In the reaction mixture calculated amount of CuPc green in the range of 1.0 to 10 mole % (with respect to monomer) was added in the presence of oxidizing agents such as ammonium per sulphate or FeCl₃ in an acidic medium. The reactions were carried out mainly at room temperature, with constant magnetic stirring. The reaction time was varied from 2 hours to 24 hours depending on the polymer. The reaction mass was poured into 400-ml distilled water (in case of polythiophene in 400-ml methanol). The obtained polymers were filtered and purified by several water washings with distilled water. Finally the polymers were dried at 80°C for 4 hrs.

Preparation of Substrates

Surface cells are essential for measuring chemical sensitivity of the polymers for sensor application. The inter-digited gold films were formed on clean glass substrates. To these films the two leads (copper wires) were attached by means of a silver paste. The polymer composite films were coated on the open area between the two electrodes.

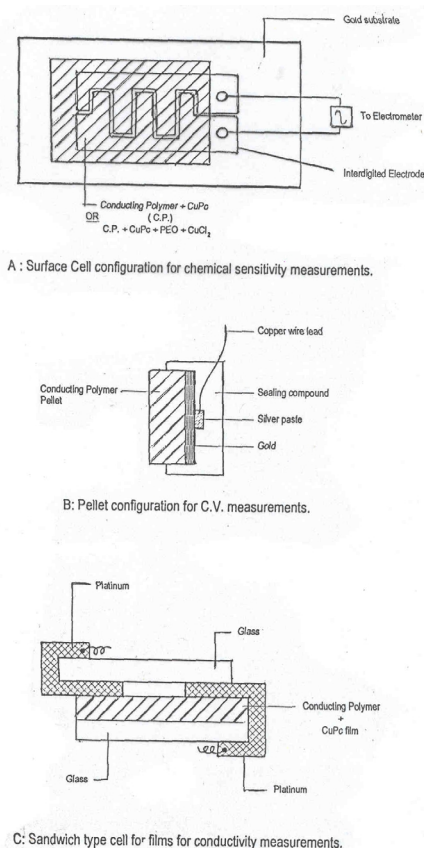


Figure 1. Schematic diagram of inter-digited surface cell used for Sensitivity Measurements.

In order to study the chemical sensitivity of modified conducting polymer powders; these were first dispersed in a film-forming matrix and then coated on the electrode. This approach was needed since the conducting polymer powders have no known solvent at room temperature. Polyethylene oxide (PEO) was chosen for dispersing the conducting polymers since it has a variety of solvents, it forms

films easily, it has low TG and T_m, which allows many types of chemical vapours to diffuse through. Earlier studies from this laboratory indicated that PEO is most appropriate for testing chemical sensitivity of conducting polyaniline for applications in sensors.

In order to make the composite films, typically 0.2 grams of PEO were taken in a petri dish to which 0.02 grams CuCl₂·2 H₂O and 2.0-ml methanol were added. The mixture was slightly warmed to form uniform greenish liquid. Desired amount of conducting polymer (ranging from 0.022 grams to 0.11 grams) was added to the solution and the mixture masticated thoroughly so as to form a paste. The fine smooth paste was then applied on the inter-digitated electrodes (Figure 1) and dried at room temperature for 24 hrs. The electrical conductivity of the sensor was monitored, by continuously recording resistivity or currents at constant potential using a stabilized DC power supply a Keithley electrometer and a fast x-y-t recorder [Lienses, Germany].

Results and Discussion

Characterization

Infrared Spectroscopy

The incorporation of phthalocyanine into the polyaniline chain was confirmed by IR studies. Figure 2 shows the IR absorption spectrum for PANI-CuPc powder samples. The curve A correspond to the sample of pure polyaniline while curves B and C correspond to the polyaniline containing 5% and 20% CuPc respectively. The characteristic IR absorption intensity due to quinoid ring at 1590 cm⁻¹ and benzoid ring at 1500 cm⁻¹ are clearly indicative of these two states in the polymer chain. The C-N stretching vibrations are appeared at 1380 cm⁻¹ and 1305 cm⁻¹ in each sample. The benzene ring C-C vibration for stretching is observed at 1463 cm⁻¹. The IR spectra of polyaniline samples, in presence of phthalocyanine exhibit new absorption peaks distinctly at 1210, 1150, 1095, 950, 900, 830, 770, 740 and 510 cm⁻¹ which are assignable to phthalocyanine skeletal vibration modes. The absence of peak at 650 cm⁻¹ assignable to C-Cl vibrations, in the functionalized polymeric samples clearly shows that polymer (polyaniline) gets attached to the phthalocyanine ring via C-Cl termination. The data represented for these polymers is well matched with the reported literature IR data for polyaniline [10] and phthalocyanine [11]. Thus, IR studies on functionalized polymer clearly gives an evidence of incorporation of phthalocyanine moieties into the polymer chain.

UV-VIS Spectroscopy

The UV-VIS spectrum of polyaniline depends strongly on its oxidation states. Figure 3 shows the optical absorption spectra (in sulfuric acid solution) of polyaniline and polyaniline functionalized with CuPc samples in the wavelength range 300-900 nm. Curves A to D corresponds to the polyaniline powder samples with CuPc content of 0, 3, 10 and 20 mole percent respectively. It can be seen that there are two new broad absorption bands occurring at 580 nm and 650 nm, which are associated with the chlorinated phthalocyanine (green) moieties [12]. Pure PANI has a broad absorption band centered at 750 nm, which is associated with the oxidation/doping of the polymer, giving rise to polaronic states within the band gap [13]. It is interesting to note that the main absorption band at 320 nm and 420 nm

of PANI are also affected by the presence of CuPc in the polymer. This can be due to higher degree of conjugation in PANI-CuPc due to the highly conjugated planar CuPc moieties attached to the main chain as well as high level of dopant present in these polymers as compared to pure PANI.

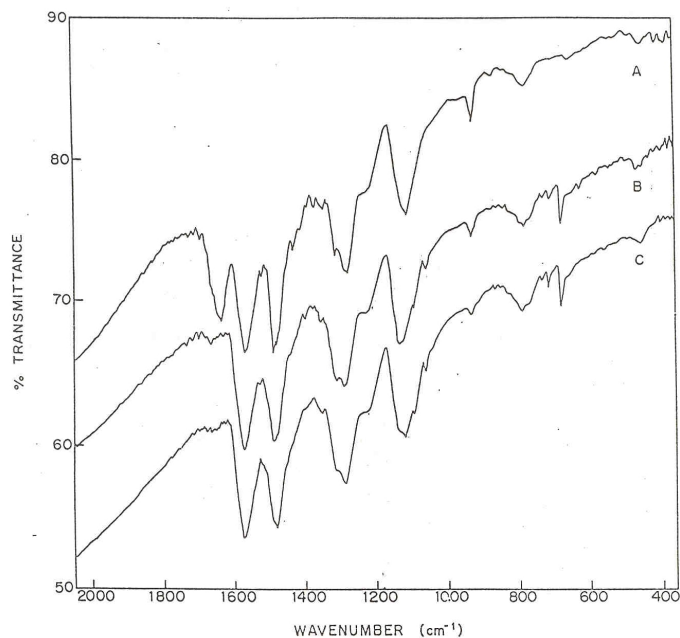


Figure 2. FT-IR spectrum of PANI-CuPc polymers (A) Pure PANI (B) PANI + 5% CuPc (C) PANI + 20% CuPc.

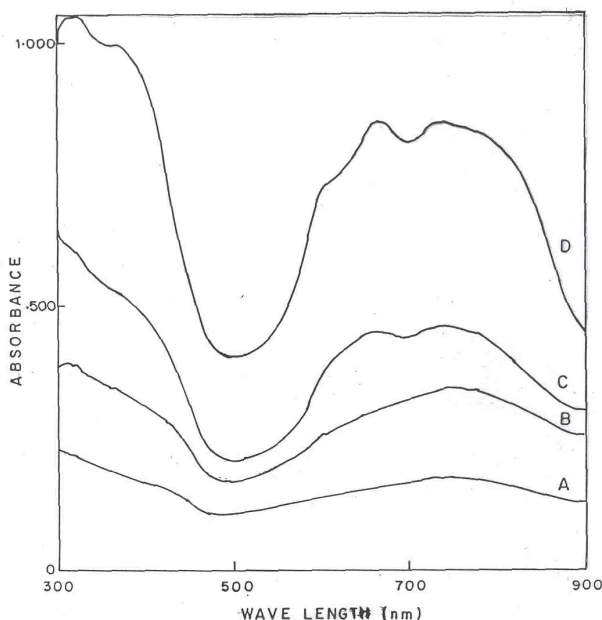


Figure 3. UV-VIS spectrum of PANI-CuPc polymers in dil. H_2SO_4 (A) Pure PANI (B) PANI + 3% CuPc (C) PANI + 10% CuPc and (D) PANI + 20% CuPc.

The gas sensing ability of pure polyaniline as well as polyaniline functionalized with phthalocyanine was checked. The pure polyaniline does not dissolve in solvents from which it can be

cast as a film. Hence, it was mixed with polyethylene oxide-CuCl₂ complex for making surface cells by applying a thin paste of polyaniline dispersed in PEO-CuCl₂ complex on inter-digited PCB [14]. Such surface cell type sensors were prepared for different compositions of PANI-CuPc. These samples were then exposed to various chemical vapours such as methanol, nitrogen dioxide and ammonia gas in a specially designed pre-evacuated glass chamber. The sensitivity factor (S) obtained for different phthalocyanine concentration in polyaniline samples are shown in Figure 4. The curves A, B and C correspond to sensitivity on exposure to the vapours of methanol, NH₃ and NO₂ respectively. The sensitivity factor S can be calculated using the expression,

$$S = \frac{R_v}{R_o},$$

where R_v is the resistance after the exposure to chemical vapour and R_o is the initial resistance. The pure polyaniline was not found to be much sensitive to chemical vapours, whereas PANI-CuPc polymers show enhanced sensitivity.

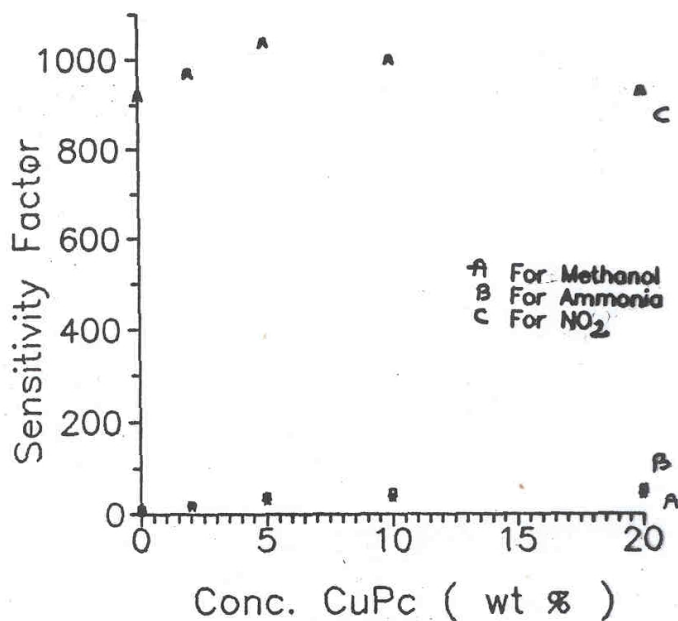


Figure 4. Plots of sensitivity factor versus CuPc concentration for (A) Methanol (B) Ammonia (C) Nitrogen dioxide vapours with PANI-CuPc/ PEO/ CuCl₂ Inter-digited electrodes

The sensitivity to methanol vapours was comparatively low (S in the range of 10 to 20) for pure polyaniline sample but almost twice ($S = 55$ to 65) for the PANI-CuPc samples. The exposure of these samples to ammonia vapour showed slightly higher sensitivity as compared to methanol. However, it is quite interesting to note the tremendous sensitivity of these samples to the vapours of nitrogen dioxide. In this case, the sensitivity factor of about 900 to 1100 was obtained depending upon the phthalocyanine concentration in the polymeric sample. The results obtained from these investigations are compiled in Table 1.

The action of chemical vapours on such sensor system would proceed as follows. Firstly the PEO-CuCl₂ matrix, which is the major component, absorbs the vapour which then has to diffuse through the

inter-domain spaces and reach the conducting polymer (polyaniline) moieties. It then interacts with the impurity states in PANI and transfer electronic charge. The transfer of electrons leads to a lowering of the potential barrier at the interface, giving rise to an increase in conductivity (or decrease in resistivity). The enhancement of sensitivity of PANI – CuPc to NO₂ is mainly due to the CuPc groups and there seems to be an optimum concentration required for maximum sensitivity.

Table 1. Sensitivity of PANI-CuPc polymers with chemical vapours.

Sr. No.	CuPc content by Wt. %	Sensitivity Factor (S)		
		Methanol	Ammonia	Nitrogen dioxide
1	0.0	11.0	6.0	100.0
2	2.0	20.0	18.0	970.0
3	5.0	40.0	30.0	1040.0
4	10.0	49.0	37.0	1000.0
5	20.0	57.0	44.0	930.0

The PPy and PPy-CuPc polymers obtained in its highly conducting form were exposed to the various chemical vapours such as methanol, ammonia and nitrogen dioxide¹⁵. The results obtained from this study are shown in Figure 5 and the data is presented in Table 2. The curve A represents the sensitivity towards nitrogen dioxide gas, whereas curve B shows the sensitivity towards the ammonia and methanol vapours. From these curves it can be seen that PPy-CuPc polymers show moderate sensitivity towards the methanol and ammonia vapours. To mention here, the ammonia vapour sensitivity is higher than that of methanol vapour. It is quite interesting to note that PPy-CuPc polymers show tremendous sensitivity towards nitrogen dioxide vapours. This very high response to nitrogen dioxide vapours can be explained as follows.

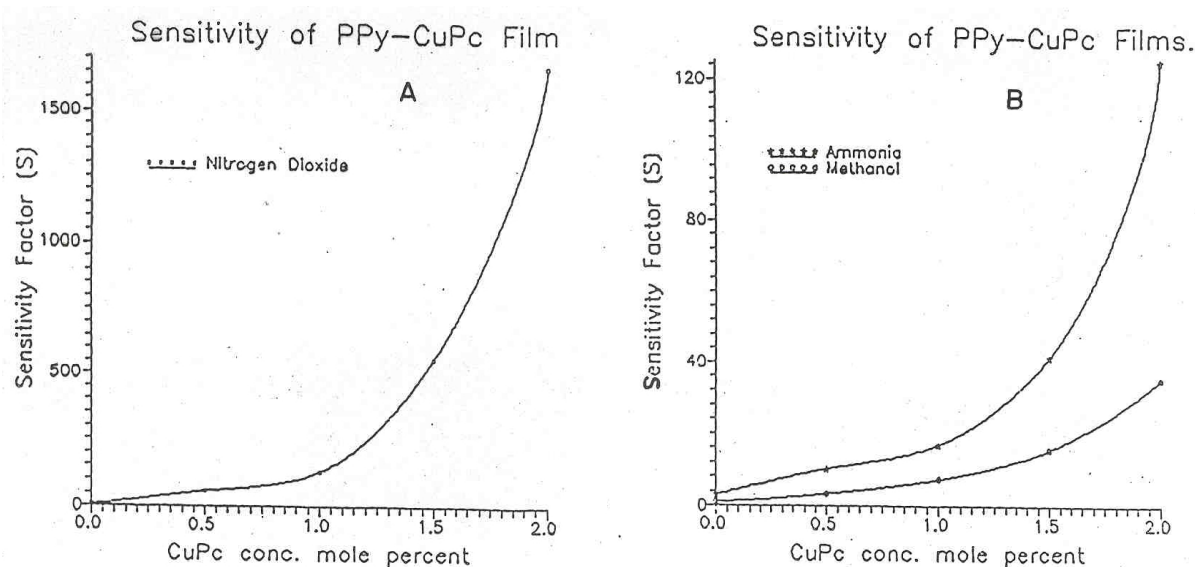


Figure 5. Plots of sensitivity factor versus CuPc concentration for PPy-CuPc polymers Nitrogen dioxide (B) Ammonia and Methanol

Table 2. Sensitivity of PPy-CuPc polymers with chemical vapours.

Sr. No.	CuPc content by Wt. %	Sensitivity Factor (S)		
		Methanol	Ammonia	Nitrogen dioxide
1	0.0	1.00	3.00	5.00
2	0.5	3.25	10.00	55.00
3	1.0	7.25	16.75	125.00
4	1.5	15.50	41.50	555.00
5	2.0	35.00	125.00	1665.00

Nitrogen dioxide was reported [16, 17], to have large effects (6 to 8 orders of magnitude) on the conductivity of phthalocyanine films. Chadwick et.al. [18], interpreted that a charge transfer complex is formed between a phthalocyanine donor and nitrogen dioxide acceptor, and the charge carriers are the holes produced in the phthalocyanine matrix. Nitrogen dioxide is π -electron acceptor, and accepted electron would delocalize over the nitrogen dioxide planar structure. Since the hole is also delocalized over the phthalocyanine structure the coulombic force between the opposite charges is weakened and charge carrier movement is facilitated. Ammonia is a competing electron donor and can displace phthalocyanine in the interaction. Thus, we can observe the less response towards the ammonia and on the other hand, tremendous response for nitrogen dioxide vapours in case of PPy polymers containing CuPc.

The various PT-CuPc polymers obtained were fabricated as a chemical sensor device using inter-digited gold films with PEO-CuCl₂-Polymer mixture. This sensor [19], was then subjected to exposure of various chemical vapours such as methanol, ammonia and nitrogen dioxide etc. The results obtained in each case are plotted in Figure 6 and the data is presented in Table 3. The figure shows the sensitivity factor versus CuPc concentration curves.

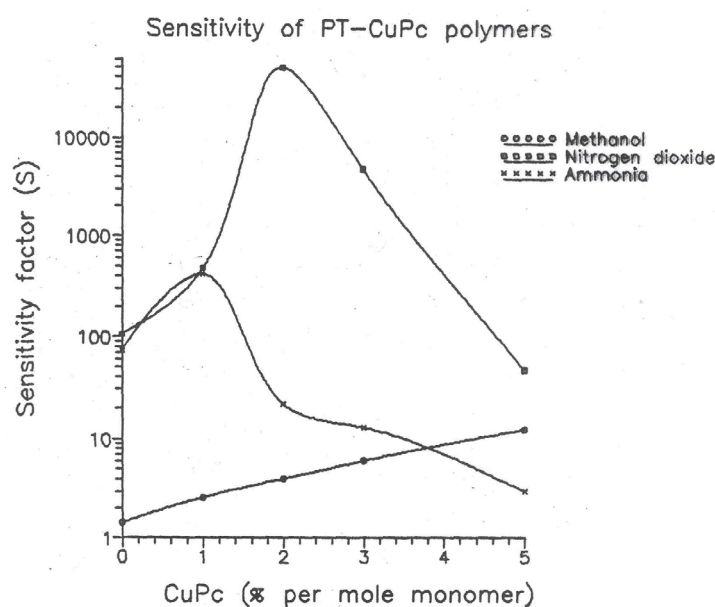


Figure 6. Plots of sensitivity factor versus CuPc concentration for Methanol, ammonia and nitrogen dioxide vapors measured with PT-CuPc/ PEO/ CuCl₂ inter-digited electrodes.

Table 3. Sensitivity of PT-CuPc polymers with chemical vapours.

Sr. No.	CuPc content by Wt. %	Sensitivity Factor (S)		
		Methanol	Ammonia	Nitrogen dioxide
1	0.0	1.43	77.33	105.26
2	1.0	2.60	416.60	476.20
3	2.0	4.00	22.00	50000.00
4	3.0	6.92	13.33	4761.90
5	5.0	12.50	3.00	47.62

The action of chemical vapours, on this composite system would proceed as follows. Firstly, PEO-CuCl₂ which is a major component would absorb the vapour, which then diffuses through inter-domain spaces and reach the conducting polymer moieties, where it would interact with the impurity states and transfer electronic charge. Transfer of electron leads to a lowering of the potential barrier at the interface, giving rise to an increase in conductivity.

It is interesting to note that sensitivity increases initially with increasing phthalocyanine content to about 3% concentration for ammonia and nitrogen dioxide vapours but then decreases for higher concentration of phthalocyanine. This peculiar behaviour can be explained as follows: The pure PT is an amorphous polymer. Through this amorphous structure diffusion of these gases would be very easy. Hence they show greater sensitivity. As the phthalocyanine content in the polymer increases, the polymer becomes more crystalline. The diffusion of the gas molecules through this well ordered crystal lattice is very difficult. Hence after certain level of CuPc concentration there is a sudden drop in sensitivity.

Conclusion

The PANI-CuPc, PPy-CuPc and PT-CuPc polymers were tested as chemical sensors by their response characteristics after exposure to various chemical vapors such as methanol, ammonia and nitrogen dioxide. The results obtained showed that these polymers have moderate sensitivity towards the methanol as well as ammonia vapors but high sensitivity towards nitrogen dioxide. It is quite interesting to note that all these polymers containing CuPc show tremendous sensitivity towards nitrogen dioxide vapors. The sensitivity factor of as high as 50,000 was obtained for PT-CuPc polymers. The sensitivity factor of 1600 was obtained in the case of PPy-CuPc polymers, whereas PANI-CuPc polymers exhibit a value of 1100 for nitrogen dioxide vapours. In comparison to this, the sensitivity factors of about 100 and 40 were obtained, when these polymers were exposed to ammonia and methanol vapors.

The very high selectivity towards the nitrogen dioxide may be explained on the basis of charge transfer complex formed between, the phthalocyanine donor and nitrogen dioxide acceptor molecules. On the other hand, ammonia becomes a competing electron donor in CuPc containing conducting polymers. The very low response towards the methanol may be explained on the basis very little

charge transfer/interaction between CuPc containing polymers and methanol. Thus, CuPc incorporated conducting polymers have much higher selectivity than their original homopolymer.

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Sample Availability: Available from the authors.