

# Highly sensitive and responsive hazardous materials sensor based on a new Fluorescent Coordination polymer

Ayman magdy<sup>1</sup>, Yousef said<sup>1</sup>, Ahmed Tayel<sup>1</sup>, Ahmed Ismail<sup>1</sup>, Ahmed Gamal<sup>1</sup>, Ramy Abdlaty<sup>2</sup>, Ahmad Baraka<sup>1</sup> and Osama Abuzalat<sup>1,\*</sup>,

<sup>1</sup>Department of Chemical Engineering, Military Technical College, Cairo, Egypt

<sup>2</sup>Biomedical Engineering Department, Military Technical College, Cairo, Egypt

Email:osama.abuzalat@mtc.edu.eg

**Abstract**– Toxic gases, such as ammonium are unsafe materials that harm safety and environmental risks. Even though many sensors have been stated for the detection of ammonium, a superficial, rapid, cost-effective sensor is still sought-after in the field. Here we establish a superficial and rapid method to synthesize a fluorescent metal–organic framework for the highly selective and sensitive detection of ammonium. Zirconium phthalic diamine framework (Zr-PH-Diamine) is synthesized. The synthesized material shows visible color changes upon exposure to ammonium from pink to yellow. In addition, fluorescence is shown under UV illumination when the Zr-PH-Diamine is exposed to ammonium. The Zr-PH-Diamine coated paper sensors show the highest fluorescence enhancing at an emission wavelength of 565 nm with ammonium concentration as low as 1 ppm. Consequently, the proposed plan not only offers a fast and convenient protocol for selective detection of ammonium but also offers great potential in practical applications, especially for industry and area where manufacture of nitric acid or hair dyes, keep public safety and decreasing environmental pollution.

**Keywords**--Coordination polymer, ammonia, sensing, fluorescence,

## 1 Introduction

The detection of ammonium is very important for keeping public safety and decreasing environmental pollution. Toxic gas, such as ammonium, are unsafe contaminants in industry and manufacture of all dyes[1]. They also position public safety risks. kits are one of the primary detection methods used at airports, ports and borders[1-5]. However, their performance degrades over time when they get tired. Ionization mass spectroscopy is another common detection method, but the bulky instruments required for this technique poses limited portability. Generally, colorimetric chemical sensors are more compact and cost-effective than desk-top mass spectrometers[6-9]. The ammonium has strong electron accepting (NH<sub>3</sub> easy convert to NH<sub>4</sub>) abilities that cause a photo induced electron transfer. This results in fluorescence enhancing or visible color changes that can be detected through different tests typically using conjugated polymers[5]. Alternatively, PCPS such as metal–organic-frameworks

(MOFs) are another purposes of materials that have shown potential for molecular storage, sensing, catalysis, and separation[10]. Lately, luminescent microporous MOFs have begun as useful materials for ammonium sensing. They are also interesting because the surface area, functionality, pore size, morphology and active center can be controlled during synthesis of PCPs.

In this paper, a fast and superficial synthesis of a fluorescent MOF has been established. We can selection the linker which contain two carboxyl groups in out and two amide groups in interstitial by manufacture the linker two mole from acid with one mole amine this enhance fluorescent properties of Zr-PH-Diamine. We identified the fluorescent inorganic metal complex. The reaction time is different to control the crystal morphology, but changes in turbidity of the solution suggest that crystals are designed after less than one minute of reaction time. The synthesized Zr-PH-Diamine are coated on a filter paper or suspended in water solution for ammonium sensing experiments. Zr-PH-Diamine displays high sensitivity and selectivity towards ammonium. Visible color changes and fluorescent enhancing are known immediately after exposure to ammonium at low concentration reach to 1ppm.

## 2 Materials and methods

### 2.1 Materials and chemical

All chemicals used in this experimental works are available in field. They were used directly from source without any purification or treatment of raw material. Most of the chemicals used in this work are stable without any explosion hazard and safe during handling because this compound not toxic at low concentration. All chemicals are of analytical grade and used without further purification such as: Phthalic acid (99% VWR), deionized water (DDW), O-Phenylenediamine (OPD, 99% VWR), Zirconium oxychloride octahydrate (98% Sigma Aldrich), ammonia by different concentration (1,10,20,50,100 ppm), acetone (99%), ethanol (98%, VWR), methanol (98%, VWR) are used.

## 2.2 Preparation of precursor solutions and synthesis of Zr-PH-Diamine.

Zr-PH-Diamine has been prepared by using different as follows: 0.1 mole of O-phenylenediamine (0.108g) with 0.2 mole of Phthalic acid (0.33g) which are dissolved in 10 ml deionized water, after two solutions completely dissolved in water then putting them in an oven for 20 minutes at temperature from 80:90 °C when color convert from colorless to yellow color these induction amide groups are formed and reaction takes place, then water is removed and amide group is produced. This amide in the linker formed the coordination polymer. It has two groups of carboxylate at its edges and in the middle there is two amide groups. Prepare the 0.1 mole of Zirconium oxychloride which take amount of Zirconium oxychloride (0.322 g) then, it is dissolved in 10 ml deionized water. Finally, we were adding the Zirconium oxychloride solution to the new linker then put the mixture in the oven at 80:90 °C temperature for 1 hours. The color is becoming pink as the result of formation Zr-PH-Diamine (coordination polymer) which zirconium plays the role of ion metal Zr+4 (node) then bonds with the linker to form the coordination polymer. Now we get the coordination polymer Zr-PH-Diamine. After separation take the drop from final solution of Zr-PH-Diamine on the filter paper which put in oven at same temperature to make the sample is dry and increase active center on surface area, put under UV at wavelength 365 nm; the sample emission light (pink color) and after put drop of ammonium the color convert from pink to yellow when wavelength is 570nm. and we just need to separate (Extract) from the liquid solution. We use the method of Settling by gravity or Centrifugal to remove the undesired liquid by suction by using syringe, then we wash the coordination polymer (PCPs) by adding distilled water and remove it after 5 minutes. The produced Zr-PH-Diamine is then dried in an oven at temperature range from 80 to 90 °C for characterization such as FTIR, XRD, SEM, etc.

## 2.3 Materials characterization techniques

A field emission scanning electron microscope (FE-SEM) is used to define and analyze the morphologies of the Zr-PH-Diamine. An X-ray diffractometer (XRD) is used to describe the crystalline structure of the Zr-PH-Diamine. Fourier Transform Infrared (FTIR) Spectroscopy instrument is used measure the transmittance spectra in the range of 4000–400  $\text{cm}^{-1}$  with a spectral resolution of 10  $\text{cm}^{-1}$ .

## 2.4 Ammonium sensing experiments

For the detection of ammonium, a portion of filter paper (36 mm in diameter) is immersed in the fluorescent Zr-PH-Diamine colloidal solution for 10 min. The filter paper then is removed from the solution and dried in oven at 80 °C for 5 min. The gravimetric calculation shows that approximately 0.2g of Zr-PH-Diamine is loaded on the filter paper. To establish its application as a paper-based sensor for ammonium detection, 1  $\mu\text{l}$  drops of ammonium solution diluted to different concentrations such as (1.10.20.50.100 ppm) are

applied at room temperature(25°C). In addition, standard solutions of methanol, ethanol, acetone are applied to test chemical selectivity. Then, the paper-based sensor is imaged with an optical camera. In addition, the fluorescent optical images below the irradiation of a UV lamp with wavelength ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ) are taken. Hyperspectral camera is used to measure the UV-vis reflectance spectra of the Zr-PH-Diamine coated paper sensor before and after applying various standard solutions of ammonium at different concentration. When you are added the different concentration of ammonium the color change from pink to yellow.

## 3 Results & discussion

In this study, the Zr-PH-Diamine material was designated as a large surface area contain large amount of voids with porous host structure and any zirconium bonded four new linkers because zirconium is Zr+4 in figure 1.

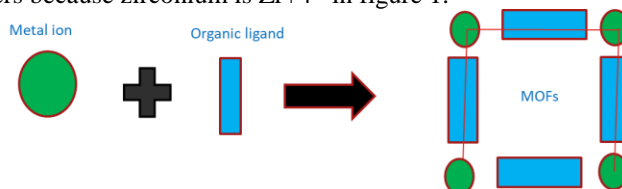


Figure. 1 Schematic diagram illustrating (Zr-PH-Diamine CP)

Zr-PH-Diamine has naturally smaller window gaps which may block the true advantage of having a larger internal void space. Really, currently studies showed that only small gas molecules could penetrate the internal void space of Zr-PH-Diamine upon application of a threshold pressure by this may be use as a storage. Zr-PH-Diamine amorphous crystals could be formed in less than one minute (via simple mixing of solution linker of phthalic acid with diamine and node of zirconium) as shown in Figure. 1 which the metal ion is called node and the organic part is called linker. The node collected number of organic linker due to type of metal.

## 3.1 Morphological and structural characterization of Zr-PH-Diamine

Graphical inspections indicate that the pure pink crystalline dried product (Zr-PH-Diamine) is obtained from the reaction of zirconium oxychloride octahydrate with linker (2 moles phthalic acid and 1 mole o-phthalaldehyde diamine) in water. Scanning electron microscopy confirms a plate like morphology of Zr-PH-Diamine, its crystal size in the range of 500 nm and shape identified as shown in Figure. 2A

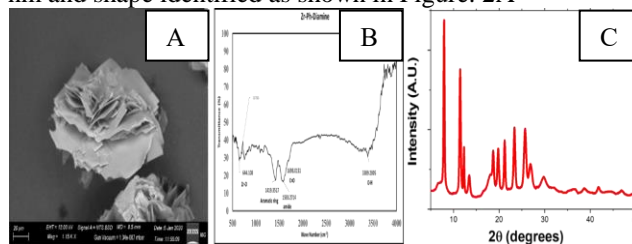


Figure. 2(A) SEM images of Zr-PH-Diamine. (B) FTIR spectrum(C) Structural characterization of Zr-PH-Diamine (pink).

Figure 2 B, The FTIR spectra of the freshly synthesized Zr-PH-Diamine are represented in library of FTIR device all function exists at accurate wavenumber. The two N-H stretching peaks observed at 3418 and 3313 cm<sup>-1</sup> corresponds to asymmetric and symmetric stretching vibration of amine group. respectively. The weak adsorption band at 3235 cm<sup>-1</sup> indicates stretching vibration of O-H group. The strong and sharp peaks moderate at 3238 cm<sup>-1</sup> indicate presence of amide groups. At 883cm<sup>-1</sup> weak absorption indicate carboxylic acid dimer. strong peaks at 1550 to 1610 indicates aromatic groups. The peak at 644cm<sup>-1</sup> indicates the presence of Zr-O bond, and the peak at 1698 cm<sup>-1</sup> indicates the presence of C=O bond. Figure 2 C presents the structural data of the pure Zr-PH-Diamine material which shows good crystallinity, the solvation of its structure is under investigation.

### 3.2 Reflectance sensing measurements

Fluorescence emission intensity is small because the concentration of ammonium is very small such as 1,10,20 ppm. the yellow color is observed by eyes at concentration 25 ppm. By this reason use some of device to detect the color at very low concentration such as hyperspectral camera. It can detect the very low concentration of ammonium and by put small amount of ammonium the curve shift left this indicate yellow color is formed and when increase the concentration of ammonium the curve shifts up due to the yellow color increase as seen in Figure.3A. The measurements indicate good linearity in the range 1-50 ppm with R2 = 0.941 as shown in figure 3.B.

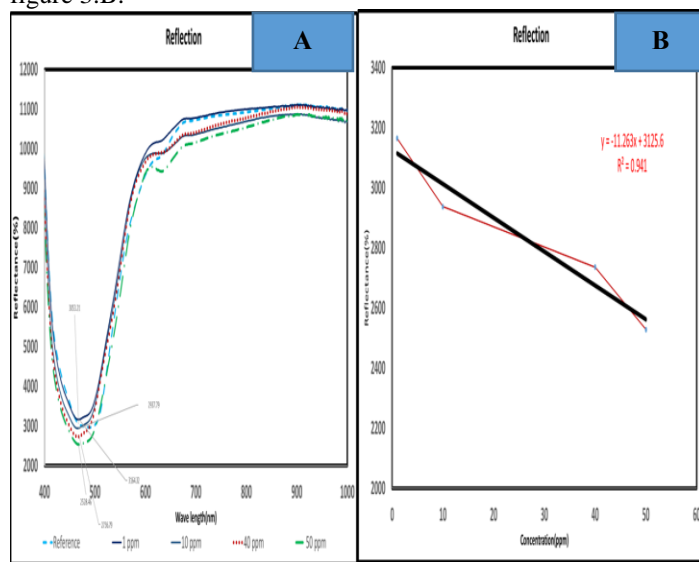


Figure 3. (A) Reflectance at different concentration of ammonium, (B) the good region which used at wavelength 470 nm

### 3.3 Visible colorimetric and fluorescent ammonium sensing

Interestingly, we detect a visible color change upon the application of different concentrations of ammonium to the Zr-PH-Diamine coated paper sensor as shown in Fig.4A. The color has been changed from pink to yellow in approximately one second which indicates an interaction between the analyte

(ammonium) and the sensing materials (Zr-PH-Diamine). It should be well-known that lowest ammonia concentration that causes visible color change which we can detect with our simple eyes is 1 ppm. As shown in Fig.4 B, with increasing ammonia concentration, absorption of light around 480 nm wavelength increases which results in color change in visible region, the curve shift left this indicated the yellow color formed and by increase the concentration of ammonium the curve shift up this indicated yellow color concentration increase and emit wavelength in region 413:568nm. The emission also has been enhanced upon ammonia addition as shown in figure 4 (B) bottom.

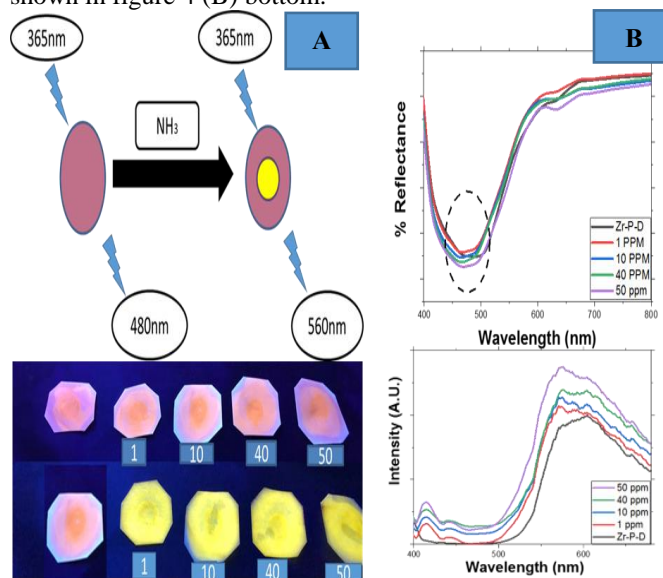


Fig. 4A Optical images of the Zr-PH-Diamine coated paper sensor as a function of ammonium concentrations. The color changes from pink to yellow with increasing concentrations of ammonium. All scale bars are 1 cm. (B) UV-vis reflectance and emission spectra as a function of ammonium concentrations.

### 3.4 Sensing mechanism

It has been described that a vapor of ammonium has an aerodynamic diameter very small which is smaller than the pore size of Zr-PH-Diamine. So, adsorption vapor of ammonium may play a major role. The ammonium sensing mechanism for Zr-PH-Diamine has been commonly described as a donor-acceptor electron transfers which the lone pair in ammonium move the Zr+4 the physical and chemical properties are changed. Moreover, the molecule of Zr-PH-Diamine when adsorbed some UV (energy), the molecule excited to upper level and take very small time in range micro-second and return to ground state in this step emission energy in wavelength is equal 480nm to give pink color. At photoexcitation of molecule sensors, the electron makes a transition to the molecular orbital of higher energy. The photo excited molecule, called the donor (Zr-PH-Diamine), has a larger band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) than the acceptor (ammonium) which has lower band gap. Both static and dynamic fluorescence enhancement are normally a matter of photo induced electron transfer between

the excited-state of the sensor, and the ground state of the explosives.<sup>7</sup> Upon contact with the ammonia compound the excited electron of molecule-sensor jumps to higher level, which is observed experimentally as fluorescence enhancing. The energy difference between HOMO and LUMO is a driving force (DF) of fluorescence shift to enhance color to bright yellow as show in figure.5.

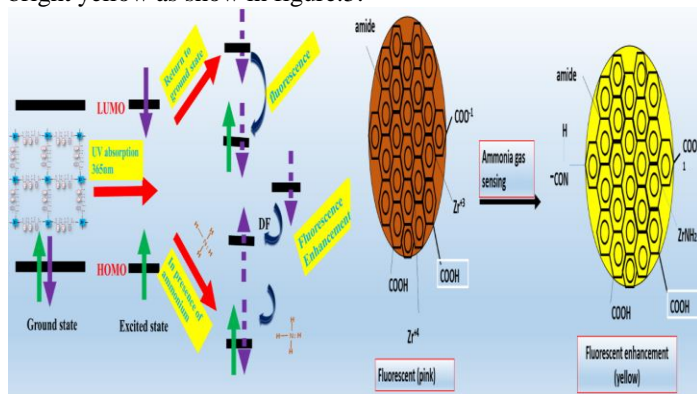


Figure.5. The mechanism of fluorescence enhancing by contact of chemical sensor (Zr-PH-Diamine) and ammonium. LUMO – the lowest unoccupied molecular orbital, HOMO – the highest occupied molecular orbital, DF – driving force. The green and brown arrows indicate the electron

#### 4 Conclusions

The Zr-PH-Diamine solution is coated on a filter paper and dried in an oven to make cost-effective, increase active center and disposable ammonium sensors. The paper-based sensors showed the most visible color change upon application of ammonium, the most fluorescence enhancing under UV irradiation ( $\lambda_{ex} = 365 \text{ nm}$ ) occurs upon application of ammonium at an emission wavelength of 570 nm. Visible colorimetric changes and fluorescence enhancing are showed at very low concentration of ammonium reach to 1ppm. In liquid phase, the fluorescence enhancing is observed by eyes down to ammonium concentration of 1 ppm. It is proposed that this strategy can be extended to nano-caging and nano-manipulation of a wide variety of light-sensitive fluorophores combined with the diverse family of MOFs for different chemical sensing applications.

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