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Synthesis of 4-Phenyl-2,6-Bis(4-Aminophenyl)Pyridine Compound and Study of Their Fluorescence Behaviour for Formaldehyde Sensing

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Abstract : The synthesis of 2,4,6-triarylpyridine derivative compounds has been done.The syntesized compound was tested as fluorescence chemosensoragainst formaldehyde as substrate and the limit of detection was determined.First step of one-pot synthesis has been done by synthesizing of 4-phenyl-2,6-bis(4-nitrophenyl)pyridine (**1**) compound between benzaldehyde and 4-nitroacetophenone. The second step synthesis has been done by reduction of nitrogroup to get 4-phenyl-2,6-bis(4-aminophenyl)pyridine (**2**) compound using HCl37% and Sn metal. The target compound was obtained in 68.9% yield.Thefluorescence assay of the solution containing sensor showed the wavelength of emission changed from 489 nm to442 nm only after the addition of HCHO in ethanol as solvent. The limit of detection byfluorescence was obtained at 6.2 ppm. Thus, the probe should be potential applications for food security.
Keywords : fluorescence, formaldehyde,pyridine, sensors.

Introduction

Formaldehyde (HCHO) is known to be the one of the chemicals in practice used as a food preservative[1].As known, formaldehyde has a serious impact on human health. International Agency for Research Cancer (IARC) clarified that formaldehyde is a carcinogen material for humans[2,3]. Early detection is important to ensure that formaldehyde residues have no harmful effects on the health of the body by controlling levels of formaldehyde contained in foods and drinks.

The standard method used for determination of formaldehyde concentration in biological materials is based on a colorimetric reaction in which the sample distillate mixed with 2,4-dinitrophenylhydrazine in concentrated hydrochloric acid is extracted in methanol and chloroform, the isolation of the chloroform layer measured by a spectrophotometer at 529 nm[4]. Other techniques such as liquid chromatography and gas chromatography have been shown to be more selective and accurate for determining formaldehyde in water[5]. However, it requires real-time sensor technology and in-situ detection simultaneously and can be reused[6,7].

As a result, the purposeful design and synthesis of efficient chemosensors to selectively detect HCHO at the environmental and biological fileds have been in recent years attracted much attention. Although a wide variety of chemical and physical sensors for HCOH sensing have been reported, most of physical methods require time-consuming of laboratorious procedures. For purposes of sensitivity, simplicity and real-time apllication, HCHO fluorescence chemosensors have become particularly attractive. Pyridine as heterocylic organic molecule able to signal the presence of fornaldehyde based on supramolecular aprroaches according to

protonation, hydrogen-bonding or formation of bond between pyridine and formaldehyde. It changes in their absorption and emission properties and these chemosensor can detect amount of formaldehyde quantitatively[8,9]. Zhou et al. (2015) has synthesized a 2-amidyl-3-(3-amidyl-1H-benzo[d]imidazolyl)pyridine compound having strong fluorescence emission for formaldehyde in an aqueous media[10].

Herein, our research group have designed 4-phenyl-2,6-bis(4-aminophenyl)pyridine that possesses a amine group and it can form imine bond when formaldehyde appear. The pyridine ring was introduced as fluorophore and the amine group as recognition moiety. The synthesis of 2,4,6-triaril pyridine generally yields high rendement and selectivity, while derivative substances have not been widely used as colorimetric and fluorescence chemosensors.

Experimental

Materials and physical methods

All reagents and solvents were comercially available at analytical grade and were used without further purification. FTIR spectra were recorded on a Shimadzu Prestige 21.GC-MS spectra were recorded on a Shimadzu QP-2010S.^{1}H NMR spectra were recorded on JEOL JNM-ECZ5000R/S1 spectrometer at 500 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane as internal standard and chloroform as solvent. UV-vis spectra were recorded on a Shimadzu D-1800 spectrophotometer. Photoluminescence spectra were performed on a Shimadzu RF-6000 spectro fluorophotometer.

Synthesis of 4-phenyl-2,6-bis(4-aminophenyl)pyridine

The synthesis route of chemosensor compound was demonstrated in **Scheme 1**. The synthesis of 4-phenyl-2,6-bis(4-nitrophenyl)pyridine (**1**) was modified from Tamami and Yeganeh (2001) procedure[11]. To ethanol solution (20 mL) of compound **1** (0.15 g, 0.38 mmol) and tin granular (0.27 g, 2.3 mmol) was stirred to a temperature of 60 °C. After that, the mixed solution was added a HCl 37% (5 mL). Then, the reaction of mixture solution was stirred at 84 °C for 2h. The reaction result was kept at room temperature and then stored in refrigerator for 24h. The reaction product was filtered and putted in a solution of sodium hydroxide solution (6.0 g/30 mL). The solution was stirred until the yellow crystal precipitate was formed, then filtered and washed with distilled water three times. The crude were purified by recrystallization using ethanol solvent to get slightly yellow crystal of chemosensor in 68.9% yield (m.p. 199.1-199.4 °C, 208 °C (Tamami and Yeganeh, 2001), ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.41-7.44 (t, 1H), 7.48-7.50 (t, 2H), 7.69-7.71 (d, 2H), 7.68 (s, 2H), 8.02-8.04 (d, 4H), 6.77-6.78 (d, 4H), 3.81 (s, 4H). IR (KBr) v: 1180 cm^{-1} (C─N), 1612 cm^{-1} (C═N), 3371 and 3425 cm^{-1} (NH_2). GC-MS for $C_{23}H_{19}N_3$ m/z 337.0 (100%)

General procedure for UV-vis experiments

A total of 2.5 mg of chemosensor compound was dissolved in 25 mL of solvents (acetonitrile, ethanol, DMSO, acetic acid, ethyl acetate). Then re-made the same solution for all solvents with the addition of 100 µL formaldehyde 37%. The two treatments before and after addition were subjected to spectral readings between 800-200 nm using a UV-Vis spectrophotometer and observed.Both treatments before and after the addition of formaldehyde was done between 800 to 200 nm spectral scan using spectrophotometer UV-Vis and observed.

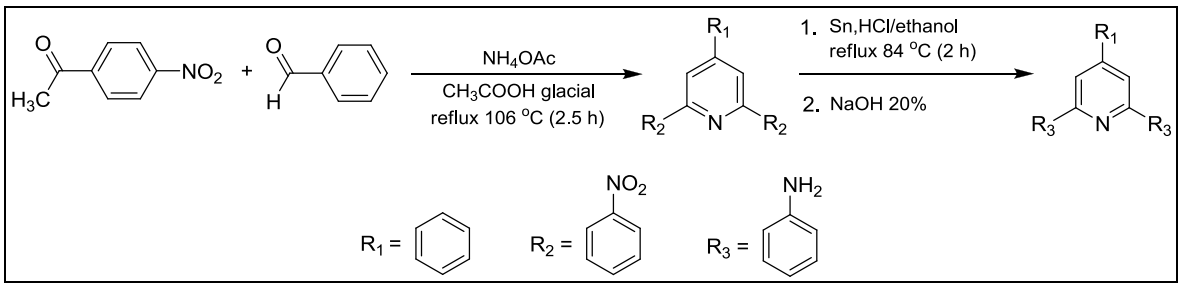
General procedure for fluorescence spectra experiments

As much as 4 mL of chemosensor solution in ethanol (2.97×10^{-6} M) was introduced into 2 vials. One of the solutions was added 50 µL formaldehyde 37%. Fluorescent spectra were performed using spectro fluorophotometer in the wavelength range of 800 to 200 nm. A total of 1.5 mL of solutions of chemosensor compound(2.97×10^{-6} M) in ethanol were included in 10 vials and then added 1 mL of formaldehyde 37% with concentration variations (0, 100, 200, 300, 400, 600, 800 , 1000, 1500, 2000, 2500 and 3000 ppm). The fluorescence intensity was calculated at the maximum excitation and emission wavelengths.

Results and Discussion

The crude was purified by recrystallization using ethanol solvent, the chemosensor compound of solid with rendemen was obtained by 68.9% and had melting point between 199.1-199.4 °C.The success of the reduction reaction of compound **1** was shown in the peak loss at 1350 cm^{-1} wavenumber as the asymmetric aryl-NO_2 strain vibration. This proves that in compound **2** does not have a nitro functional group. The molecular ion has an M^+ value equal to the mass of the theoretical molecule of chemosensor molecule.Ingole et al. (2010) reported substituted 2,4,6-triaryl pyridine compounds were analyzed using GC-MS having M^+ molecular ions appearing as base peak[12].^{1}H NMR showed the total hidrogen atoms in each molecule there are a number of 19 hidrogen atoms (6.7-8.0, C-H arom., 15H; 3.8, NH_2, 4H).

Test of chemosensor compound was dissolved in acetonitrile, ethanol, DMSO, acetic acid andethyl acetate solvent and showed a colorless appearance except in acetic acid showing yellow color (**Figure 1**). Then compared with the addition of saturated formaldehyde in same solvents, showed that only ethanol which can give the appearance of peaks with the difference that can be observed before and after the addition of formaldehyde in the visible region.



Scheme 1. Synthetic procedures for chemosensor compound

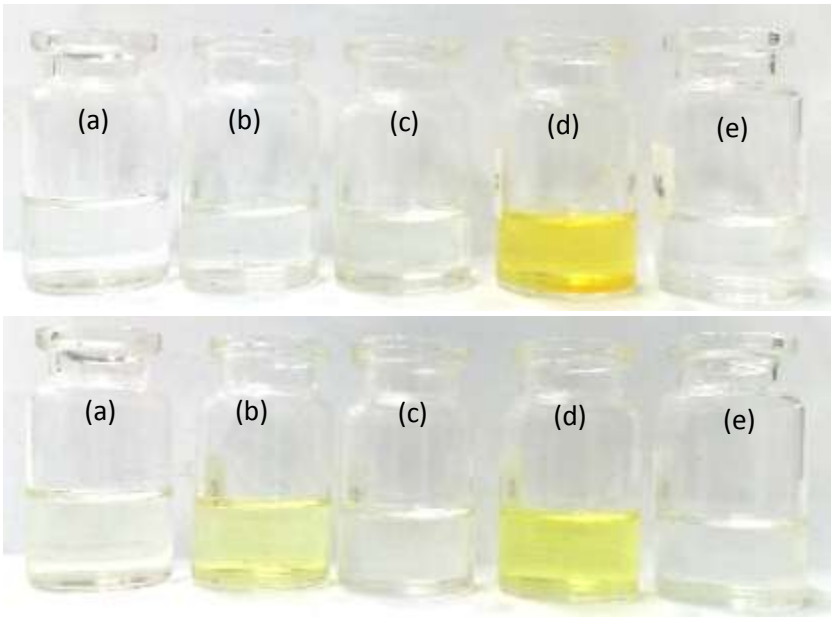
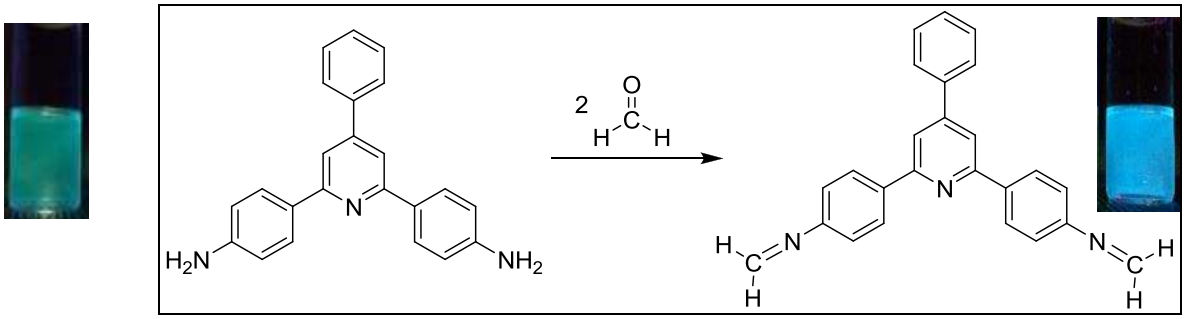


Figure 1. Solutions of chemosensor compound (above) and after addition of formaldehyde (below) in the solvent: (a) acetonitrile; (b) ethanol; (c) DMSO; (d) acetic acid; (e) ethyl acetate

Chemosensor molecular structure has a primary amine group, the group can be used as a substrate binding side for formaldehyde to bind to form an imine covalent bond (**Scheme 2**). The imine is formed by the reaction between the primary amine functional group as the nucleophile attacks the carbonyl aldehyde group in formaldehyde.



Scheme 2. Sensing mechanism

The chemosensor test on formaldehyde as a substrate using spectrophotometer was performed 3-dimensional reading between 800-200 nm to determine the maximum wavelength of excitation and emission states. The reading results in **Figure 2** and **Figure 3**, showed that chemosensor solution has a maximum wavelength of 305 nm excitation and 489 nm emission. While the chemosensor solution with adding formaldehyde has changed the maximum wavelength of emission to 442 nm.

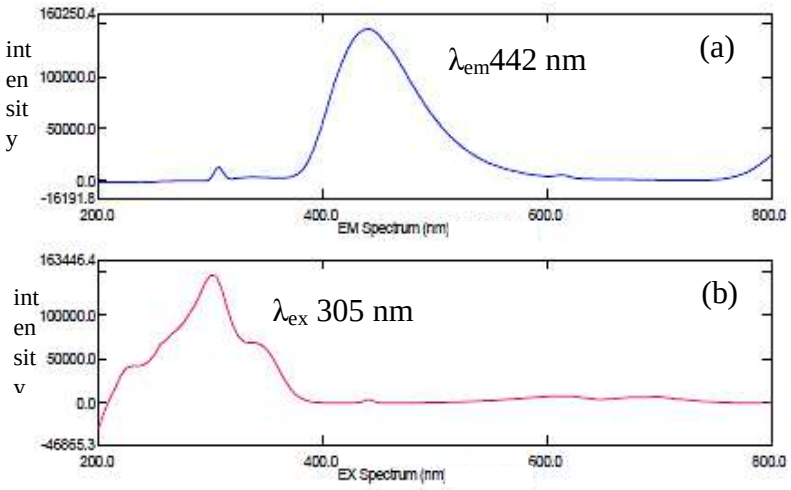


Figure 2. Chemosensor solution (2.97×10^{-6} M) in ethanol: a) emission spectra, b) excitation spectra

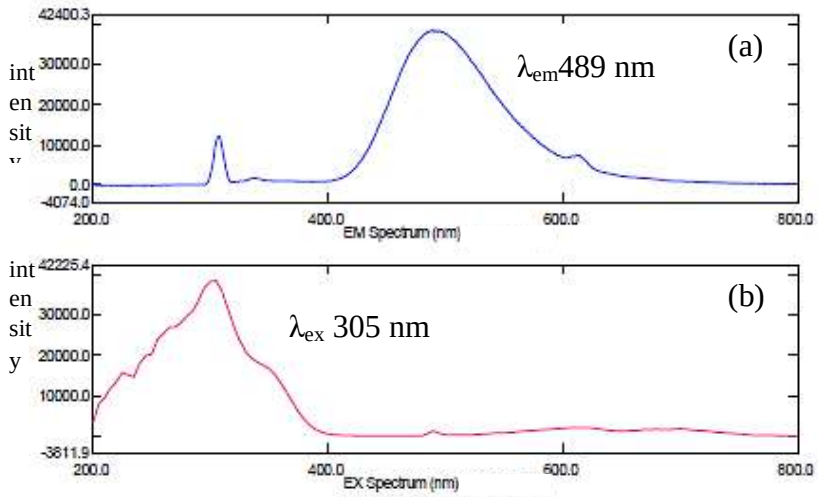


Figure 3. Chemosensor solution (2.97×10^{-6} M) in ethanol upon adding of 50 µL of formaldehyde 37% : a) emission spectra, b) excitation spectra.

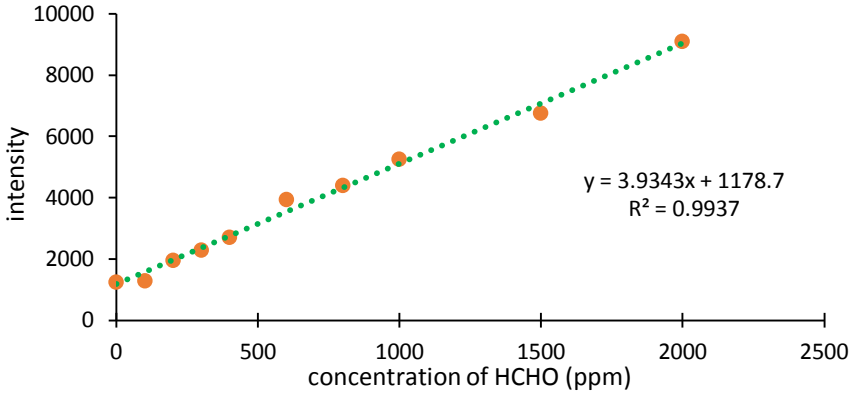


Figure 4. Fluorescence detection limit spectra of chemosensor (2.97×10^{-6} M) in ethanol solution upon adding of concentration of HCHO (6.2 ppm)(w/v).

Chemosensor compound in the ethanol solvent made standard curve obtained slope value of 3.9343 $mg^{-1}L$ and obtained standard value deviation of blank solution of 8.141. Then based on the determination of the value of detection limit obtained value of 6.2 ppm (w/v).

Conclusion

In conclusion, we have presented a rapid and efficient chemosensor for formaldehyde, which showed highly sensitivity fluorescence recognition for HCHO in ethanol solutions. The fluorescence spectra showed difference appearance between before and after addition of formaldehyde to chemosensor solution about emission wavelength shift 489 to 442 nm. The sensor demonstrates the detection limit of the sensor to HCHO on fluorescence response is down to 6.2 ppm, which is lower than the ATSDR of 10 ppm. We believe that these characteristics of chemosensor through formation of imine bond, make it attractive for molecular modifications and applications as fluorescence sensor for HCHO.

Acknowledgements

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