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# New synthesis of *N*, *N'-bis*-(1*H*-pyrrol-2-yl-methylene)-benzene-1, 2-diamine and *N*, *N'-bis*-(1*H*-pyrrol-2-yl-methylene)-benzene-1, 4-diamine in the presence of argon or $Zn^{2+}$

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**Abstract:** Considering the importance of aromatic amines derivatives due to their biological activities, new synthesis of *N*, *N'-bis*-(1*H*-pyrrol-2-yl-methylene)-benzene-1,2-diamine and *N*, *N'-bis*-(1*H*-pyrrol-2-yl-methylene)-benzene-1,4-diamine from the reaction of aromatic amines due to their biological activities and pyrrolcarbaldehyde in the presence of argon or zinc ion is reported.

**Keywords:** Zinc; 1, 2 and 1, 4-Diaminoaniline; Fluorescent sensor; *N*, *N*'-bis-(1*H*-pyrrol-2-yl-methyleamin.

## Introduction

Fluorescent sensors are an indispensable tool for visualizing or monitoring metal ions in real-time and real-space at a molecular level without any special instrumentation and are applicable in many fields such as medical diagnostics, environmental control, living cells and electronics [1]. Zinc ion is an important divalent cation in biological systems and plays important roles in a human body, influencing DNA synthesis, microtubule polymerization, gene expression, apoptosis, immune system function and the activity of enzymes such as carbonic anhydrate and matrix metalloproteinase [2]. Moreover, zinc ion is also a contributory factor in neurological disorders such as epilepsy and Alzheimer's diseases [3]. Consequently, investigation focused on detecting $Zn^{2+}$ of low concentration in vivo has attracted increasing interests [4]. Detection of $Zn^{2+}$ in materials and environments is also of importance [5]. $Zn^{2+}$ sensors based on the Fura-2 and Indo-1 family of $Ca^{2+}$ of small molecular size have recently been reported [6,7].

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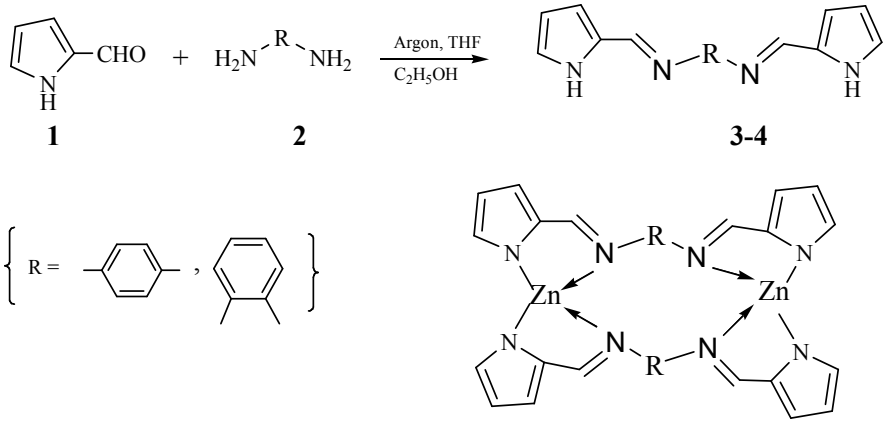
However, these probes require UV excitation, which may damage to cells, this presents auto fluorescence problems when applied in vitro. Available $Zn^{2+}$ with excitation in the visible range is not ratiometric in response characteristics [8-11]. The most common class of fluorescent sensors for metal ions is based on photo induced electron transfer (PET) quenching mechanisms [12].

Jin Shi Ma et al. has recently involved in the study of self-assembly of so-call pyrrol-shiff base or pyrrol-2-yl-methyleneamine ligands with metal ions and their properties as fluorescent $Zn^{2+}$ sensors [13-15].

In this paper, we report the synthesis of several *N*, *N'-bis*-(1*H*-pyrrol-2-yl-methylenediamine) ligands, such as *N*, *N'-Bis*-(1*H*-pyrrol-2-yl-methylene)-benzene-1,2-diamine and *N*, *N'-Bis*-(1*H*-pyrrol-2-yl-methylene)-benzene-1,4-diamine **3-4** from the reaction of 2-pyrrolcarbaldehyde and aromatic amines and their properties in the presence of argon and Zinc ion as fluorescent $Zn^{2+}$ sensors (Scheme **1**).




**Scheme 1.**

## Results and discussion

The reaction between 2- pyrrolcarbaldehyde **1** and aromatic amines or ethylene diamine **2** at room temperature leads to *N*, *N'-bis*-(1*H*-pyrrol-2-yl-methylene)-benzene-1,2-diamine and *N*, *N'-bis*-(1*H*-pyrrol-2-yl-methylene)-benzene-1,4-diamine (**3-4)** in the presence of argon and Zinc ion as fluorescent $Zn^{2+}$ sensors (Scheme **1**). The structure of compounds **(3-4)** was evaluated based on detailed spectroscopic studies. Thus, the IR spectrum of compound **(3)** showed peaks at 3228, 1624 and 1551 $cm^{-1}$ indicating the presence of NH, C=C and C=N functional groups, respectively. After addition of $Zinc^{2+}$, the IR spectrum of compound **3** showed peaks at 1650 and 1544 $cm^{-1}$ indicating the presence of C=C and C=N bonds. The $^1H$ NMR spectrum of **3** showed the presence of aromatic protons in the region of δ=6.27, 6.71, 7.10, and 7.23 ppm. The proton of the *CH*=N is in the region of δ=8.39 and NH is in the δ=9.96 ppm.

The spectral data of compound **4** are described. In IR spectrum, stretching frequencies at 3444, 1647 and 1575 $cm^{-1}$ confirmed the presence of NH, C=C and C=N bonds. After addition of $Zn^{2+}$, the IR spectrum of compound **4** showed peaks at 1649 and 1544 $cm^{-1}$ indicating the presence of C=C and C=N bonds. The $^1H$ NMR spectrum of **4** showed the presence of aromatic protons in the region of δ=6.29, 6.80, 6.99 and 7.23 ppm. The chemical shift of NH=C*H* proton is in the region of δ=7.54 and NH is in the δ=10.96 ppm. In the $^{13}C$ NMR spectral of compounds **3-4**, peaks in the range of δ 109.9-149.9 correspond to the aromatic carbons.

In conclusion, we have reported the synthesis of several new *N*, *N'-bis*-(1*H*-pyrrol-2-yl-methylenediamine) ligands, such as *N*, *N'-bis*-(1*H*-pyrrol-2-yl-methylene)-benzene-1,2-diamine and *N*, *N'-bis*-(1*H*-pyrrol-2-yl-methylene)-benzene-1,4-diamine **3-4** from the reaction of 2- pyrrolcarbaldehyde and aromatic amines at room temperature, and their properties in the presence of argon and Zinc ion as fluorescent $Zn^{2+}$ sensors (Scheme **1**).

*UV-Vis:*

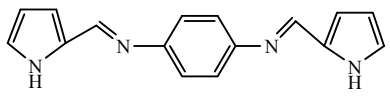
In THF, compounds **3-4** absorbed light at 352 and 347 nm, respectively, and exhibited no fluorescence (Table **1**). However, upon addition of $Zn^{2+}$ to the solution, their absorptions were red-shifted to 413 and 401 nm, respectively (Table **1**, Fig.**1** and **2**).

Fig. **1** Upon addition of $Zn^{2+}$ to the solution, their absorptions were red-shifted to 413 and 401 nm, respectively

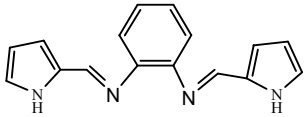
Table 1: Photophysical properties of ligands and complexes with $Zn^{2+}$ in THF

| Compound | Absorption |
|---|---|
| **3** | 369 |
| **3'** | 421 |
| **4** | 344 |
| **4'** | 400 |

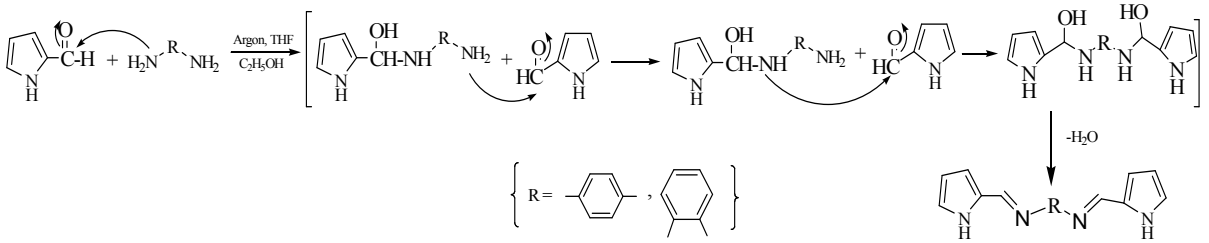
Fig. 1




**3**




**4**



**Scheme 2.**

Mechanistically, the reaction starts with the 2-pyrrolcarbaldehyde **1** and aromatic amines **2** at room temperature in the presence of argon and Zinc ion, in good yields (Scheme **2**).

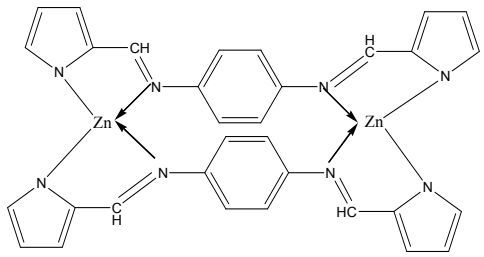


**Fig. 2**

## Experimental

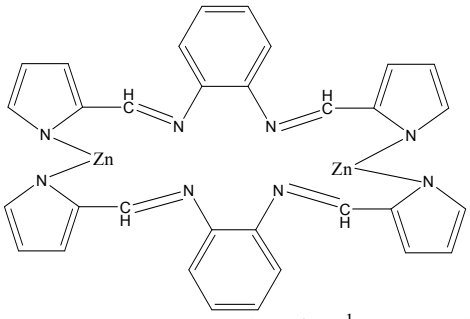
All compounds in these reactions were obtained from Merck co. and were used without further purification, mp: Thomas-Hoover capillary. FT-IR spectra: Bruker VERTEX-70. $^{1}$H and $^{13}$CNMR spectra: Bruker DRX-500Avance instrument; in $CDCl_3$ or acetone at 500 and 125 MHz, respectively.

**General procedure for the synthesis of N, N'-bis-(1*H*-pyrrol-2-yl-methylenediamine) 3-4:**

Diamine (1 mmol) in solution of acetone (30 ml) was added with stirring at room temperature to a solution of 2-pyrrolcarbaldehyde (0.48g, 2 mmol) in ethanol (40 mmol). The reaction mixture was stirred 48 h under argon protection during which red Crystals were observed. The crystals were filtered off and washed with tetrahydrofuran.

***N*, *N'-bis*-(1*H*-pyrrol-2-ylmethylene)-benzene-1,4-diamine 3:**

Red crystal, (0.19 g, 80%), mp: in 200 ºC was



decompose, IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3238 (NH), 3051 (CH, aromatic) 1639 (C=C), 1528 (CH=N), cm$^{-1}$. $^{1}$H NMR (300.1 MHz, TMS, Acetone): δ= 10.92 (2 H, *s br,* 2 NH), 8.46 (2 H, *s*, 2 CH=N), 7.23 (2 H, *s br*, 2 H pyrrol), 6.70 (2 H, *s br*, 2H pyrrol), 6.27 (2 H, *s br*, 2 H pyrrol), ppm. $^{13}$C NMR (75.4 MHz, TMS, acetone): δ 149.9,149.2, 131.6, 123.5, 121.9, 116.3 and 110.1 (C aromatic).

***N*, *N'-Bis*-(1*H*-pyrrol-2-ylmethylene)-benzene-1,2-diamine (4):**

Red oil, (0.19 g, 80%), IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3246 (NH), 3051 (CH, aromatic) 1639 (C=C), 1528 (CH=N), cm$^{-1}$. $^{1}$H NMR (500.1 MHz, TMS, $CDCl_3$): δ= 10.96 (2 H, *s br,* 2 NH), 7.54 (2 H, *s br*, 2 CH pyrrol), 7.23 (4 H, *dd*, 4 H ph), 6.99 (2 H, *s br*, 2H pyrrol), 6.80 (2 H, *s br*, 2 CH=N), 6.29 (2 H, *s br,* 2 CH pyrrol), ppm. $^{13}$C NMR (75.4 MHz, TMS, $CDCl_3$): δ 146.2, , 137.5, 122.8, 122.3, 121.3, 114.2, 110.2 and 109.9 (C aromatic).

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