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# A simple colorimetric chemosensor with highly performance for detection of cyanide and copper ions and its practical application in real samples

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ABSTRACT

Two novel and simple azo-based compounds with electron-withdrawing and electron-donating groups (M1 and M2) were synthesized by the diazotization procedure. The synthesized compounds were then applied for detection of important ions in aqueous solutions of acetonitrile. Sensor M1 with electron-withdrawing group (EWG) showed distinct colorimetric responses towards $CN^-$ (light yellow to red) and $Cu^{2+}$ (light yellow to dark yellow). Through titration experiment, the detection limit (LOD) of M1 for $CN^-$ and $Cu^{2+}$ ions sensing were found to be nano molar (nM) level. Job's plot based on spectroscopic data showed the complexes formation between M1 and ions has the stoichiometric ratio of 1:1 (M1-$CN^-$ and M1-$Cu^{2+}$). In addition, the binding constants for M1 towards $CN^-$ and $Cu^{2+}$ were determined using the Benesi-Hildebrand equation. Furthermore, the M1-based test papers strips were successfully used to the rapid detection of $CN^-$ ions in semi-aqueous medium. Importantly, sensor M1 was applied to detect $CN^-$ and $Cu^{2+}$ in real water samples and apple seeds samples. However, for M2, containing electron-donating group (EDG), no clear color changes were observed in the presence of investigated ions.

## 1. Introduction

In recent years, metal cations and anions play essential roles in environmental, chemical and biological systems. There has been a lot of interest to monitoring and measuring various ionic species due to their important effects in many industrial and environmental processes [1–5]. Among various ions, cyanide and copper are well known for their important effects on both environment and biological systems. Cyanide and its derivatives are significant environmental pollutants with high toxicity. Cyanide is also well known for its toxic effects in biological systems. The high toxicity of cyanide is due to the binding of it with iron in cytochrome c oxidase. This interaction prevents transport of electrons from cytochrome c oxidase to oxygen [6–10]. In addition, the sources of cyanide are different and it can be exist in various forms in the environment. Cyanide is produced naturally in the environment by various organism and plants. Incomplete combustion during forest fires is believed to be a major environmental source of cyanide. In addition, the various industries are responsible for the cyanide present in toxic wastes. Generally, cyanide is essential ion in a variety of fundamental industrial processes [11–15]. On the other hand, among the various cations, copper is essential to human health and it plays important roles in different physiological processes. It must be obtained from food and drinking water each day. It is an essential factor for the normal formation of the brain and nervous system. However, the abnormal uptake of copper ions can lead to liver or kidney damage, gastrointestinal disturbance, dermal or eye irritation and the nerve disorder such as Alzheimer's disease, Menke's disease and Wilson's disease [16–20]. Due to the public health concerns, monitoring the concentration of essential ions in environmental samples and finding practical ways for simultaneous detection of them is essentially important.

In recent years, several detection methods have been developed for sensing of copper and cyanide in various processes [21–23]. However, the introduction and development of a suitable method for ion sensing in real samples is vital for scientists. As a low-cost and convenient technique, the chemical sensors are a very promising method for the detection of ions. Particularly, multifunctional colorimetric sensors for the detection of two or more ions with different mechanisms have received attention due to their easy operation, instant response time, remote control and multiplicity of measurable parameters [24–33].

The objective of the present work is to develop multifunctional colorimetric sensors for the naked-eye detection of important ions with high sensitivity and low detection limits. Therefore, we have now prepared a selective and sensitive colorimetric probe based on 2-

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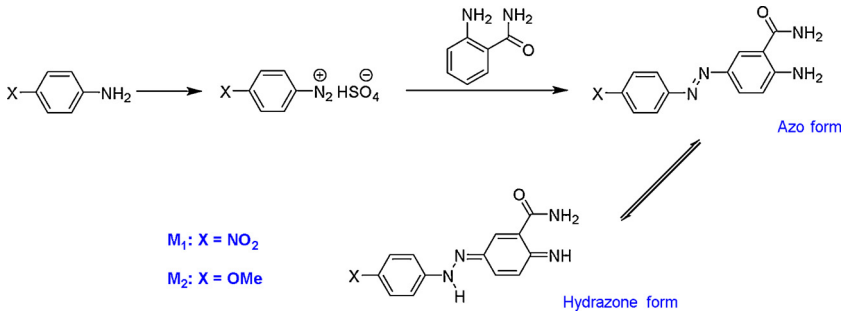


**Scheme 1.** Synthetic rote of sensors M1 and M2.

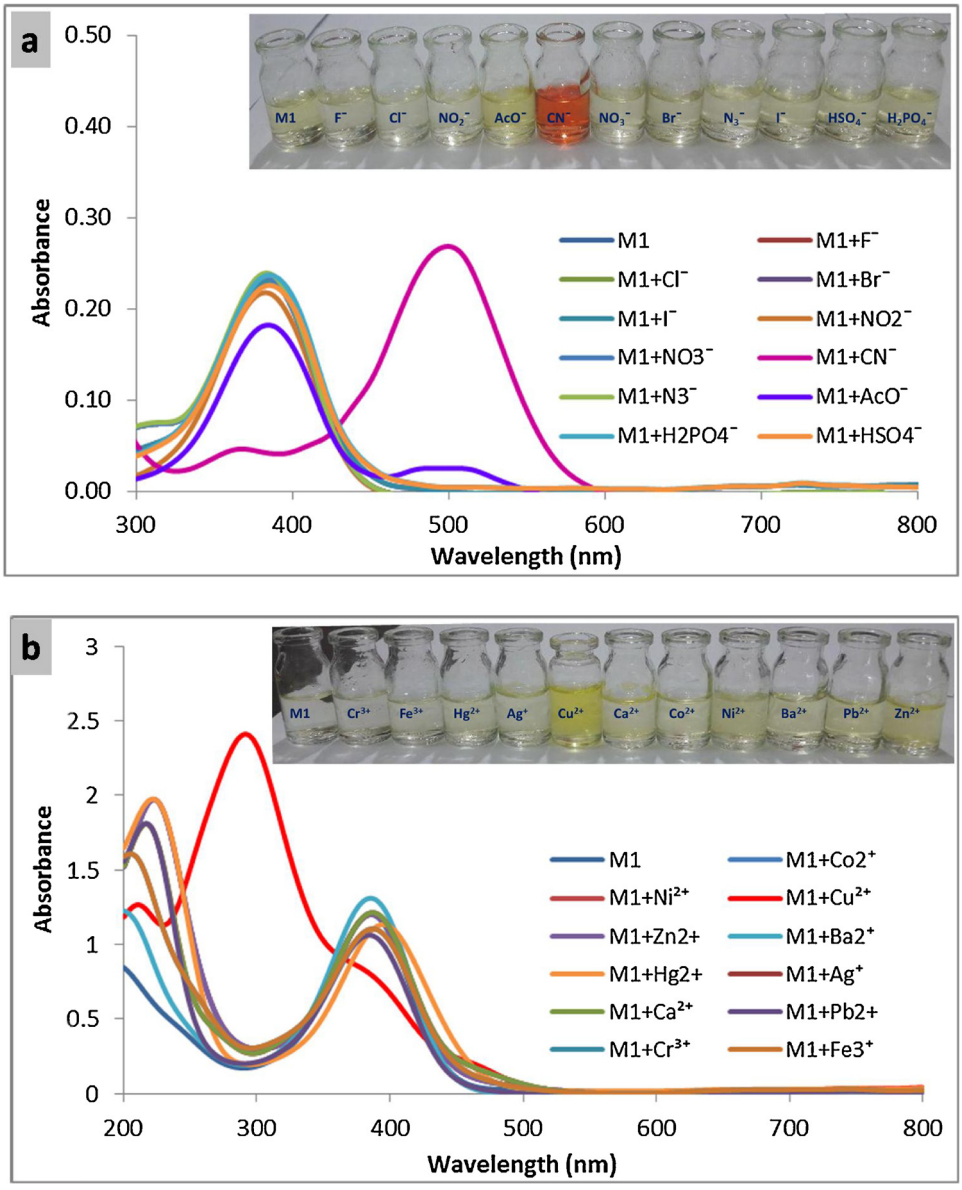


**Fig. 1.** Addition of various anions and cations to the solutions of the sensor M1 in $CH_3CN$-$H_2O$ (9:1, v/v) solution.

aminobenzamide for optical detection of $CN^-$ and $Cu^{2+}$ ions in aqueous solutions of acetonitrile. The production of filter papers (test kits) for the measurement of ionic species without any spectroscopic instrumentation can provide useful information for related users.

## 2. Experimental

### 2.1. Materials and equipment

All the chemicals were prepared from Sigma-Aldrich and Merck Chemical companies and used without further purification. The anion solutions were prepared by dissolving their sodium salts in distilled