

# Chemical sensor using metal-organic complex: Preparation, characterization and application for highly selective detection of cyanide ions in mixed aqueous-organic media



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## ABSTRACT

In this study, a novel metal-organic hybrid material (MO1) was designed and synthesized for the detection of  $\text{CN}^-$  ions. The spectral analyses by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, CHN and TGA satisfactorily confirmed the structure of MO1. The sensor MO1 was applied as colorimetric probe for sensing of cyanide ions in aqueous solutions of dimethyl sulfoxide. MO1 with electron withdrawing group at organic ligand showed high selectivity for detection of cyanide over other interfering anions. Interaction of MO1 with cyanide provides obvious colorimetric change from red to violet, enabling easy detect with the naked eye. In addition, the sensing details were evaluated using UV–vis spectroscopy. Furthermore, the detection limit of chemosensor toward  $\text{CN}^-$  ions was found to be  $5.52 \mu\text{M}$ . Moreover, probe MO1 can be used for selective sensing of cyanide based on the obvious color changes in real samples.

## 1. Introduction

The rapid growth of organic and inorganic pollutants in various industrial processes, and discharge without effective treatment, has created serious health and safety problems for the environment. Cyanide and its derivatives are significant environmental pollutants with high toxicity. The sources of cyanide are different and it can 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 [1–6]. On the other hand, cyanide is essential ion in a variety of fundamental industrial processes [7–10]. Therefore, the efficient detection of trace amounts of cyanide, as toxic pollutant, in the various samples is very important for protection of human health and environment.

In recent years, various analytical and spectroscopic methods have been developed to detect cyanide ions in various chemical and biological systems, but the problems associated with the high cost and low sensitivity have restricted their uses [11–16]. Recently, colorimetric chemical sensors as optical methods have attracted much attention because of the cost-effectiveness, sensitively, selectively, real-time monitoring, lack of equipment required, and suitable visual detection [17–21]. In our continuing research and considering the essential role

of chemical sensors in ion sensing, we focused our study on the development of metal-organic complexes for the detection of cyanide ions. Metal-organic complexes are hybrid materials consisting of metal ions or and organic ligands. These materials are widely used for a variety of practical applications such as gas storage, separation, optic, electronic, catalysis, recognition, and host-guest systems [22–25]. In general, the structural classification of metal-organic materials is greatly dependent upon the functionality and the geometry of the organic ligands used in the coordination process. Due to their pore structure and pore surface functionality, the area of metal-organic materials has become one of the fastest growing fields in chemistry. These hybrid materials are promising candidates for the detection applications because of their specific electronic and optical properties, and high surface area [26–29]. Herein, we report a new stable metal-organic complex (MO1), constructed through the reaction of  $\text{CuCl}_2$  with an azo-based organic ligand under reflux conditions. In addition, we report the sensing properties of MO1 toward investigated anions. The results were demonstrated the MO1 is able to selectivity detect cyanide over other investigated anions, which is potentially useful in the sensing of toxic cyanide in real samples.

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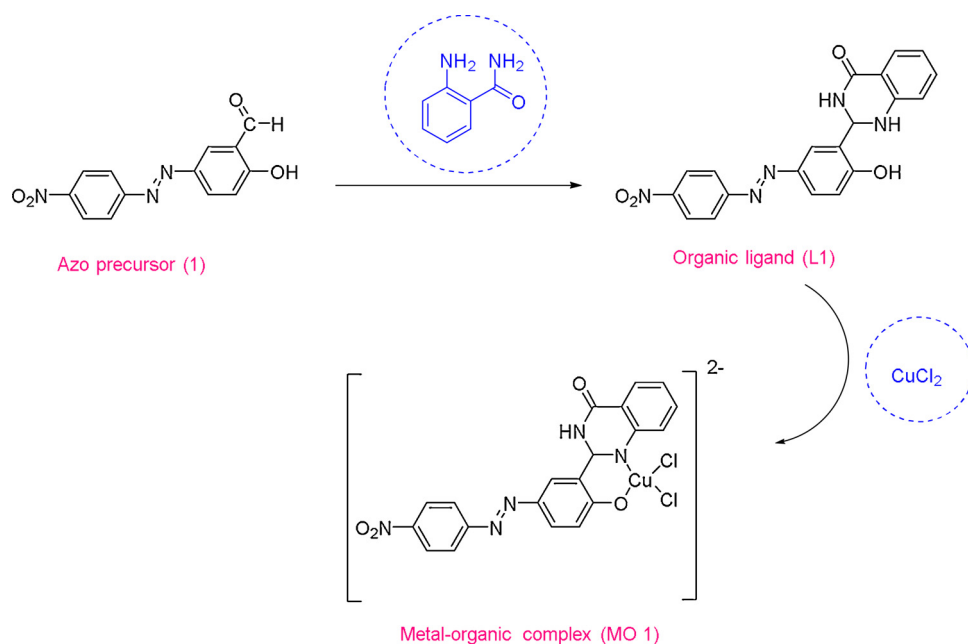
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Scheme 1. Synthesis route of the probe MO1.

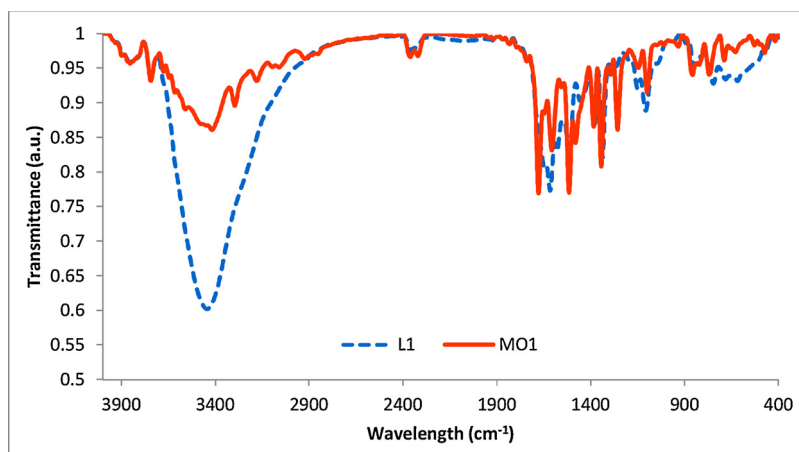


Fig. 1. FT-IR spectra of complex MO1 and organic ligand L1.

## 2. Experimental

### 2.1. Materials and equipment

All chemicals used in this study were obtained from Sigma-Aldrich and Merck Chemical companies and used without further purification. The anion solutions ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $CN^-$ ,  $N_3^-$ ,  $AcO^-$ ,  $HSO_4^-$ ,  $H_2PO_4^-$ ,  $PO_4^{3-}$ ,  $HS^-$ ,  $S^{2-}$ ,  $CO_3^{2-}$ ,  $SCN^-$ ,  $ClO_4^-$ ) were prepared by dissolving their sodium salts in distilled water ( $5.0 \times 10^{-2}$  M). To prepare standard solution from MO1, the sensor was dissolved in dimethyl sulfoxide to afford  $6.0 \times 10^{-5}$  M. Distilled water was used throughout the sensing test. The UV-vis absorption spectra were recorded using a Pharmacia Biotech Spectrophotometer in the range 200–800 nm. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu 8400 FT-IR spectrophotometer.  $^1H$  NMR and  $^{13}C$  NMR spectra were obtained on a FT-NMR (400 MHz) Bruker apparatus, and the chemical shifts are expressed in  $\delta$  ppm using TMS as an internal standard and  $J$  values are given in Hz. Thermal stability of MO1 was performed by thermogravimetric analyzer (TG 209 F1 Iris, NETZSCH) in nitrogen atmosphere at a scan rate of 20 K/10 min from 25 °C to 500 °C. The CHN analyses were performed on a Vario-ELIII elemental

analyzer.

### 2.2. General procedure for the synthesis of MO1

In order to prepare metal-organic chemosensor, firstly, quinazolinone-based precursor, as organic ligand (L1), was prepared in good yield according to methods previously described [30,19]. Then, a mixture of organic ligand (1.0 mmol),  $CuCl_2$  (1.0 mmol) and methanol (10 mL) was refluxed in a 25 mL round-bottom flask for 6 h. After cooling to room temperature, the crystals of MO1 are filtered and washed several times with methanol and water.

**MO1:** Red crystal, yield 92%, M.p. > 350 °C, FT-IR (KBr)  $\nu$   $cm^{-1}$ : 3467, 3308, 2921, 1678, 1607, 1515, 1383, 1346, 1260, 1107. Elemental analysis calculated for  $C_{20}H_{13}Cl_2CuN_5O_4$  (%): C, 46.04; H, 2.51; N, 13.42. Found (%): C, 46.31; H, 2.74; N, 13.09.

**L1:** Red Solid, yield: 96%, M.p. 277–279 °C, FT-IR (KBr)  $\nu$   $cm^{-1}$ : 3491, 1646, 1592, 1518, 1452, 1386, 1338, 1283, 1145, 1094, 853, 757, 694.  $^1H$  NMR (400 MHz, DMSO- $d_6$ , ppm, 298 K):  $\delta$  6.09 (s, 1H, CH), 6.71 (t,  $J = 7.4$  Hz, 1H, ArH), 6.82 (d,  $J = 7.6$  Hz, 1H, ArH), 6.94 (s, 1H, NH), 7.12 (d,  $J = 8.8$  Hz, 1H, ArH), 7.27 (t,  $J = 8.0$  Hz, 1H, ArH), 7.68 (dd,  $J = 1.6$  Hz, 1H, ArH), 7.91 (dd,  $J = 2.8$  Hz, 1H, ArH),

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