



# The anion recognition properties of a novel hydrazone based on colorimetric and potentiometric studies



Divya Singhal, Neha Gupta, Ashok Kumar Singh \*

Department of Chemistry, Indian Institute of Technology-Roorkee, Roorkee 247667, India

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## ABSTRACT

A novel hydrazone, 1,3-bis (2-formylphenoxy) propane bis (2,4-dinitrophenyl hydrazine) (S) has been synthesized and characterized by the NMR, IR, CHNS, UV–Vis, Raman, TEM and XPS analysis. Upon the addition of monohydrogen phosphate (MHP) ion, sudden color change from light yellow to dark violet has occurred. The binding constant of S-MHP was determined by Hill plot. Hydrazone also showed potential response with MHP ion. A number of polymeric membrane electrodes (PME) and coated graphite electrode (CGE) were also fabricated and found that the CGE has revealed better results in comparison to PME in terms of the detection limit of  $7.58 \times 10^{-9}$  mol L<sup>-1</sup> and Nernstian response.

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## 1. Introduction

The ion sensing by using an organic system has huge importance in the field of biology, agriculture, environmental analysis. Phosphate has great role in many biological, environmental, clinical and industrial systems. Due to the wide uses of phosphate fertilizers in agricultural soil, the phosphate level in the water has increased in recent years, which may cause water impurities [1,2]. So there is a need to prepare a phosphate selective electrode for monitoring the  $\text{HPO}_4^{2-}$  ion in aqueous solution and this will become very significant in many research fields because phosphorous is a crucial mineral for the human body and other living organisms [3].

In recent years, scheming of such an organic system for the naked eye detection of ions and fabrication of ion selective electrode is of great attention, as there are easy to use devices that permit fast and precise determination of chemical species at extremely low concentration [4]. There is some more analytical method for measurement of cations and anions at low concentration including UV–Vis and fluorescence studies.

**Abbreviations:** ISE, ion selective electrode; MHP, monohydrogen phosphate; PME, polymeric membrane electrode; CGE, coated graphite electrode; DBP, dibutylphthalate; TBP, tri-*n*-butylphosphate; DOP, dioctylphthalate; 1-CN, 1-chloronaphthalene; o-NPOE, *o*-nitrophenyloctylether; BA, benzyl acetate; HTAB, hexadecyltrimethylammonium bromide; CTAB, cetyltrimethylammonium bromide; PVC, poly(vinyl chloride); DMSO, dimethyl sulphoxide; THF, tetrahydrofuran; S, 1,3-bis(2-formylphenoxy) propane bis (2,4-dinitrophenyl hydrazine).

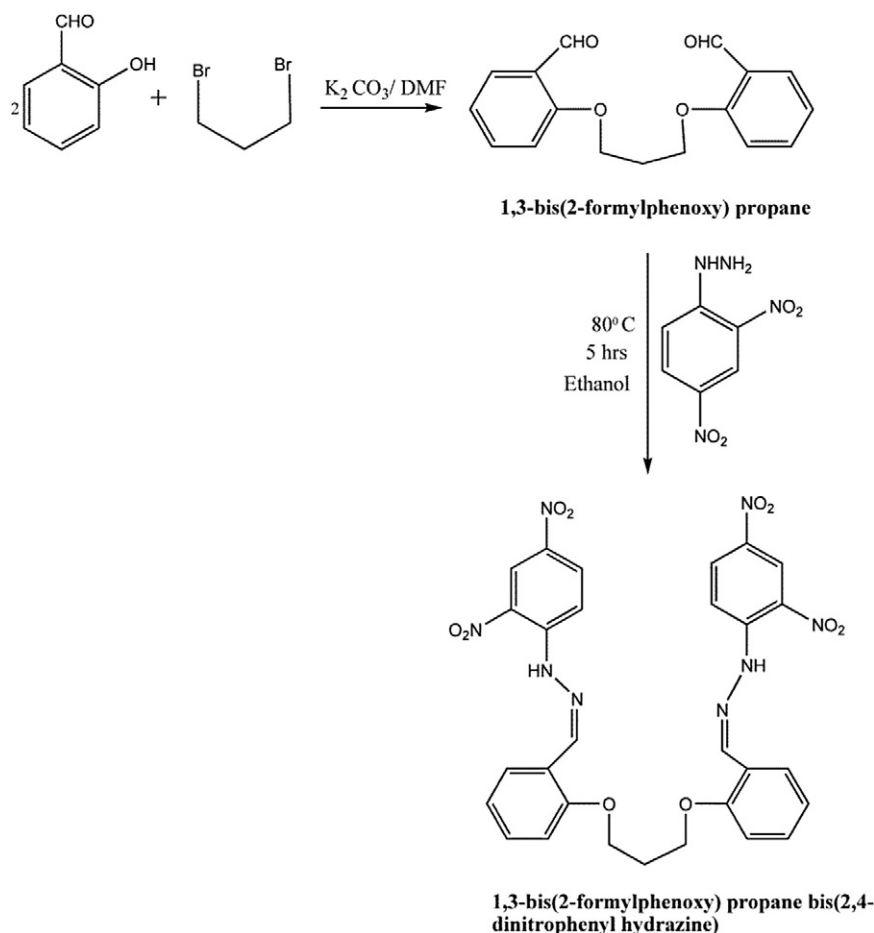
\* Corresponding author.

E-mail address: [akscyfy@iitr.ernet.in](mailto:akscyfy@iitr.ernet.in) (A.K. Singh).

The fabrication of chemosensor for anion sensing based on supramolecular concept naturally requires a mean to output the sensing in quantifiable and measurable change. Chemosensor responds visual detection without using any spectroscopic instrumentation to immediately indicate qualitative information, while absorption spectroscopy provides quantitative information [5]. The presence of any specific group in the organic system is more applicable in anion sensing. The chromophoric and electron withdrawing nitro group of hydrazone is more useful in anion sensing. The hydrazone interacted with anions due to the hydrogen bond formation. However, multiple hydrogen-bond interactions were also necessary in high-affinity anion binding sites. Colorimetric sensors for various anions and cations have been reported [6–15].

Many literatures have been reported in the field of phosphate selective electrodes. In 1988, Glazier et al. have reported the monohydrogen phosphate (MHP) membrane electrode based on the dialkyl and diaryltin derivatives [16]. In 1997, Liu et al. have reported monohydrogen phosphate (MHP) membrane electrode based on tribenzyltin oxide [17]. In 1997, Antonisse et al. used uranyl salophen for MHP selective sensor [18]. In 2000, Fibbioli et al. used zwitterionic bis (guanidinium) ionophore in membrane electrode [19]. In 2003 M.R. Ganjali et al. used vanadyl salophen for determination of trace amount of monohydrogen phosphate by using PVC-based membrane [20]. In 2007, F. Kivlehan et al. proposed membrane electrode for monohydrogen phosphate based on calyx [4]arene anion receptor [21]. In 2011 N.R. Modi et al. used phenyl urea substituted calix [4] arene for monohydrogen phosphate (MHP) ion selective membrane electrode [22].

In this work, we have described a novel monohydrogen phosphate colorimetric and potentiometric sensor. The proposed sensor describes here the selectivity for MHP ion over other anions, such as sulfate, sulphite, acetate, fluoride and chloride.



**Scheme 1.** Synthesis of hydrazone 1,3-bis(2-formylphenoxy) propane bis(2,4-dinitrophenyl hydrazine) using 1,3-bis(2-formylphenoxy) propane.

## 2. Experimental

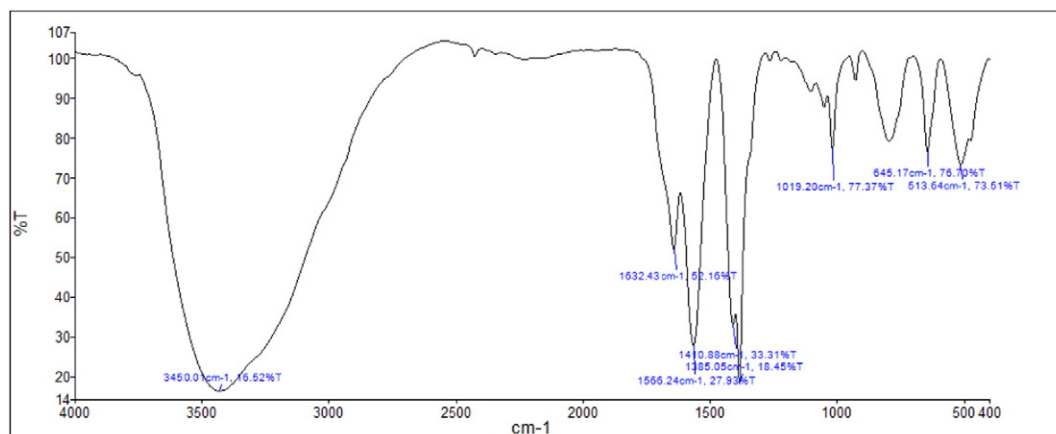
### 2.1. Reagent

For the fabrication of polymeric membrane electrode, poly(vinyl chloride) (PVC) of high relative molecular weight, hexadecyltrimethylammonium bromide (HTAB), cetyltrimethylammonium bromide (CTAB), dibutylphthalate (DBP), tri-*n*-butyl phosphate (TBP), benzyl acetate (BA), dioctyl phthalate (DOP), *o*-nitrophenyloctyl ether

(*o*-NPOE), tetrahydrofuran (THF) and anion salts were all of analytical reagent grade and purchased from Merck. 1,3-dibromopropane, salicylaldehyde and 2,4-dinitrophenylhydrazine were purchased from Sigma-Aldrich.

### 2.2. Apparatus and instrumentation

IR spectra were recorded with a Perkin Elmer FT-IR 1000 spectrophotometer as films between KBr. The UV-Vis spectra of the compounds



**Fig. 1.** FT-IR spectra of hydrazone.

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