



ISSN: 0976-3031

Available Online at <http://www.recentscientific.com>

CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research  
Vol. 8, Issue, 7, pp. 18172-18178, July, 2017

**International Journal of  
Recent Scientific  
Research**

DOI: 10.24327/IJRSR

## Research Article

### SYNTHESIS OF 3-SUBSTITUTED-1, 5-DIARYLFORMAZANS FOR THEIR USE AS NAKED EYE CHEMICAL SENSOR FOR DETECTION OF $\text{Cu}^{2+}$ AND $\text{Hg}^{2+}$

Sanjeev Kumar\* and Rajeev Sharma

Department of Chemistry, Multani Mal Modi College, Patiala-147001, Punjab (India)

DOI: <http://dx.doi.org/10.24327/ijrsr.2017.0807.0463>

#### ARTICLE INFO

##### Article History:

Received 15<sup>th</sup> April, 2017  
Received in revised form 25<sup>th</sup>  
May, 2017  
Accepted 23<sup>rd</sup> June, 2017  
Published online 28<sup>th</sup> July, 2017

#### ABSTRACT

A differently substituted series of synthesised and characterized 3-cyano-1,5-diarylformazans and 3-nitro-1,5-diarylformazans have been investigated for their colorimetric response towards metal ions  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Hg}^{2+}$  in THF-water (2:3 v/v) using 10mM borate buffer and cetylpyridinium chloride (CPC) as surfactant. It has been found that the transition metal ion particularly  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  respond very well in aqueous solutions between pH 9-10 to the compounds under study.

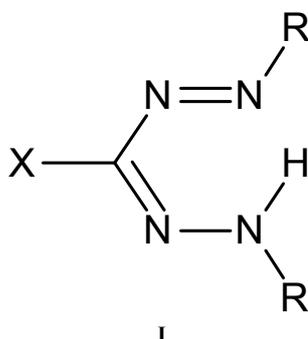
##### Key Words:

Formazans, Tetrazolium salts, Naked eye chemical sensor,

Copyright © Sanjeev Kumar and Rajeev Sharma, 2017, this is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution and reproduction in any medium, provided the original work is properly cited.

#### INTRODUCTION

Formazans fall under the category of azo compounds having the general formula  $[\text{R}-\text{N}=\text{N}-\text{C}(\text{X})=\text{N}-\text{NH}-\text{R}]$  (Structure- 1) where R is an aryl or heterocyclic moiety and X=SH, OH, CN,  $\text{NO}_2$ , or substituted aryl group etc. and form a distinct class of organic compounds with characteristic properties.



Formazan dyes are intensely colored artificial chromogenic products obtained by the reduction of tetrazolium salts by dehydrogenases and reductases. They exhibit a wide variety of colors from dark blue to deep red to orange. The reduction of tetrazolium salts in plant tissue at pH 7.2 was first demonstrated in 1941<sup>1</sup>. They have since been used in biochemistry, cytochemistry and histochemistry<sup>2-5</sup>. The dehydrogenases essential for oxidation of organic compounds

and cellular metabolism reduce the tetrazolium salt to red TPF (1, 3, 5-triphenylformazan) while it remains as white TTC in areas of necrosis since these enzymes have been either denatured or degraded. Thus formazans have found utility in autopsy pathology. Formazans are also used to detect biological redox system in blood serum, in living cells, tissues, tumors and bacteria<sup>6</sup>. Many compounds of this type have also marked antiviral action, antimicrobial action, anti-cancer drugs and antineoplastic properties. The conversion of tetrazolium salts into metallizableformazan dyes can also be employed in photographic development processes<sup>7-8</sup>. Many metallized form azans are well suited as dyes for textile materials on the account of their coloring strength and good fastness. Another area of application is detection of bacterial capacity in industrial wastewater and determination of dehydrogenase activity in sludge<sup>9</sup>. They can also be effective in photographic emulsions as antifogging agents. Their bicyclic forms can be used as dyes in inks for ink-jet printing<sup>13</sup>. They find application as optic recording dyes to provide good light stability to optical recording layers and elements<sup>11-13</sup>.

A sensor is a system that undergoes a transformation in its molecular structure or a state upon stimulation by any form of energy.<sup>14</sup> This change in the molecule is employed to analyze the stimulant.

\*Corresponding author: Sanjeev Kumar

Department of Chemistry, Multani Mal Modi College, Patiala-147001, Punjab (India)

Chemical sensors find extensive application in our every day life to detect the toxicants and contaminants as shown below in table 1:

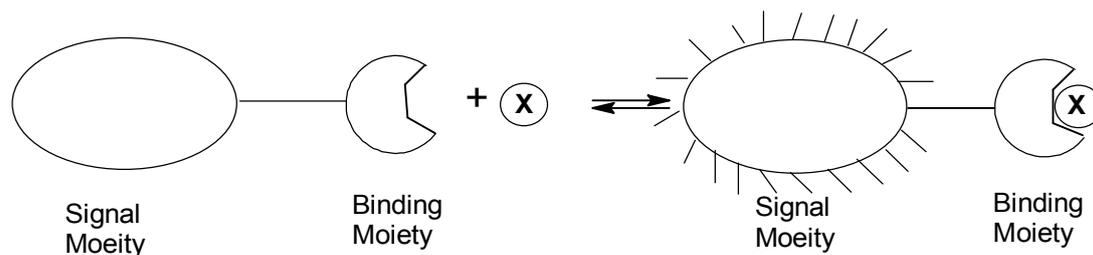
**Table 1** Applications of chemical sensors in everyday life

Applications	Examples of substances detected
Food	Biological chemicals, fungal toxins, bacteria, pH.
Medicine	Biomolecules, ketones, urea, glucose, $Na^+$ , $K^+$ , $Ca^{2+}$ , pH.
Water Treatment	pH, $O_2$ , $O_3$ , $H_2S$ , $Cl_2$ .
Environment	$CO_2$ , $H_2S$ , pH, $NO_2$ , $NH_3$ , heavy metal ions.
Industry	Toxic gases, combustible gases, $O_2$ , indoor air quality.
Petrochemical/Hydrocarbons	$HC_x$ , conventional pollutants.
Steel	$O_2$ , $H_2$ , CO and conventional pollutants.
Military	Explosives, propellants
Aerospace	$O_2$ , $H_2$ , $CO_2$ and humidity

Many neutral and ionic species due to their diversified utility have intruded in our daily life like physiology, medical diagnostics, catalysis, heavy industry, agriculture and environmental chemistry. Heavy metal ions such as  $Ag^+$ ,  $Cu^{2+}$ ,  $Co^{2+}$ , and  $Hg^{2+}$  etc. have invaded different fields due to their utilitarian value.<sup>15-21</sup> Different cations and anions are used in industry, farming and pose a threat to human health and environment.

The development and exploitation of chemical sensors is the newly emerged field in chemical sciences for last two decades. According to the widely accepted definition of a chemical sensor, "Cambridge definition", the chemical sensors may be defined as the miniature devices that be used to get real time and on-line information for the presence of the specific ionic species or compounds in even complex samples. Chemical sensors often employ specific transduction techniques to provide analyte information.<sup>22,23</sup>

The working of chemosensor can be depicted as shown in following figure 1.



**Fig. 1** Schematic diagram representing the binding of an analyte by a chemo sensor

Various forms of mercury exist in elemental or metallic and inorganic and organic (e.g. methyl mercury) forms, to which people may be exposed through their occupation and diet. These forms of mercury differ in their degree of toxicity and in their effects on the nervous, digestive and immune systems, and on lungs, kidneys, skin and eyes. Once in the environment, mercury can be transformed by bacteria into methylmercury, it bioaccumulates in the environment, biomagnifies in fish and shellfish.

Elemental and methylmercury are toxic to the central and peripheral nervous systems. The inhalation of mercury vapour

can produce fatal effects on the nervous, digestive and immune systems, lungs and kidneys. The inorganic salts of mercury may damage gastrointestinal tract, and may induce kidney toxicity if ingested. Mercury poisoning can lead to several diseases, including, Hunter-Russell syndrome and Minamata disease. Inhalation, ingestion or dermal exposure of different mercury compounds leads to neurological and behavioural disorders including tremors, insomnia, memory loss, neuromuscular effects, headaches and cognitive and motor dysfunction.

Mercury is contained in many products, including batteries, measuring devices, such as thermometers, barometers, electric switches and relays in equipment lamps (including some types of light bulbs), dental amalgam (for dental fillings), skin-lightening products and other cosmetics and pharmaceuticals. Due to higher toxicity of mercury, great interest has been devoted to the development of chemosensors.<sup>24-33</sup>

Copper is an essential trace element in plants and animals. The human body contains copper at a level of about 1.4 to 2.1 mg per kg of body mass. Copper facilitates ion uptake in human beings thus copper deficiency can produce anaemia-like symptoms. Its deficiency leads to neutropenia, bone abnormalities, hypopigmentation and impaired growth, increased incidence of infections, osteoporosis, hyperthyroidism, and abnormalities in glucose and cholesterol metabolism. Conversely, Wilson's disease<sup>34-36</sup> causes an accumulation of copper in body tissues. Severe deficiency can be found by testing for low plasma or serum copper levels. The alterations in cellular level of copper have also been associated with Prion, Alzheimer's and Parkinson's disease.<sup>37-39</sup> Copper ion can also lead to complete liver damage in infants.<sup>40-41</sup> Because of such hazardous life threatening impact of copper, the recognition of copper with the aid of chemosensors has attracted much attention over the last few years.<sup>42-44</sup>

## Experimental Section

### General Procedure for Synthesis of 3-Cyanoformazans

To an ice cold solution of aniline (40 mmol), 12 M concentrated hydrochloric acid (10 mL) and water (10 mL), sodium nitrite was added (3.00 g, 43 mmol) in small portions drop wise while stirring the reaction mixture continuously. After 30 min of stirring, the mixture was slowly added to a second solution containing cyanoacetic acid (1.70 g, 20 mmol), sodium hydroxide (8.00 g, 200 mmol), and water (100 mL) at 0°C over a 30 min period. After the addition was complete, the reaction mixture was stirred further for one hour in an ice bath

and then left overnight in refrigerator. The resulting solution was filtered to remove a black solid, and the organics extracted into dichloromethane (3 x 250 mL). After removal of the solvent the resulting dark orange solid was purified via column chromatography (neutral alumina, dichloromethane). All the 3-cyano-1,5-diarylformazans were synthesized by following the same procedure.

### Materials and Instruments

All solvents and reagents were obtained commercially and were used without further purifications. All organic solvents were purified using standard procedure.  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectra were recorded on Bruker Advance II 400 MHz Spectrometer. The IR spectra of the ligands were recorded in KBr and in carbon tetrachloride, on Cary eclipse 630 FTIR spectrophotometer. The UV visible spectra were recorded on UV-Vis Thermo Fischer Scientific 2600 spectrophotometer with 1.0cm path length cells and matched dual silicon photodiode detectors. These photo physical measurements were performed in THF/water (2:3 v/v). The mass spectral studies were performed on LC/MS 6200 series Q-TOF/6500 series, B.05.00 (B5042.0) version. The inorganic salts  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $(\text{CH}_3\text{COO})_2\text{Cu}$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $(\text{CH}_3\text{COO})_2\text{Hg}$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{CH}_3\text{COONH}_4$ ,  $(\text{CH}_3\text{COO})_2\text{Ca}$ ,  $(\text{CH}_3\text{COO})_3\text{Cr}$ ,  $(\text{CH}_3\text{COO})\text{Li}$ ,  $(\text{CH}_3\text{COO})_2\text{Zn}$ ,  $(\text{CH}_3\text{COO})_2\text{Ni}$ ,  $(\text{CH}_3\text{COO})_2\text{Co}$ ,  $(\text{CH}_3\text{COO})_2\text{Mn}$ ,  $(\text{CH}_3\text{COO})_2\text{Mg}$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{AgNO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$  were purchased from Merck.

### Spectroscopic Measurements

The stock solutions of concentration  $10^{-3}\text{M}$  formazan (FZN) were prepared in THF + water (2:3 v/v) solution. The solutions of the given compounds were freshly prepared by diluting the stock solution to the required concentration. The aqueous solution of the various metal ions  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Hg}^{2+}$  with 100 equivalent concentration were also prepared. These metal ions were added to the solution of the given compounds containing THF + water (2:3 v/v) the surfactant Cetylpyridinium chloride (CPC) containing 10 m mol borate buffer, maintained at  $\text{pH}=9.3$ . To 10 ml of the measuring flask, 3 ml of the solution of the compound prepared in THF + water (2:3 v/v) was added, then to the solution 1.0 ml of 10 m mol of the borate buffer was added along with 2ml of .01% of the surfactant (CPC). To the above solution 100 equivalent of aqueous solution of given metal ion was added making the total volume upto 10 ml. The UV visible spectra of above solution was scanned from 200-600 nm (UV-visible region) with the help of UV-visible spectrophotometer.

## RESULT AND DISCUSSION

### Photophysical Properties

The stock solution ( $10^{-3}\text{M}$ ) of 3-cyano-1,5-p-anisylformazan (FZN) was prepared in the THF+water (2:3 v/v) solution. Then the solution was diluted to  $1.5 \times 10^{-5}\text{M}$  resulting in the yellow color solution. The UV-visible spectrum of the above solution was recorded in the range 200-600 nm by using UV-visible spectrophotometer. Two strong absorption peaks were observed at 254 nm and 474 nm along with a weak band at 312 nm.

### Naked Eye Detection of $\text{Cu}^{2+}$ and $\text{Hg}^{2+}$

The absorption spectra of the formazans under study 3-cyano-1,5-p-anisylformazan for the various metal ions have been studied by UV-visible spectroscopy. We selected aqueous solutions of some metal ions, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Hg}^{2+}$  with 100 equivalent concentration and added them to the receptors taken separately in different test tubes. Apart from  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ , the other metal ions did not show any significant change in the absorption spectra (Fig. 3). The formation of  $(\text{FZN})_2\text{-Cu}^{2+}$  complex is accompanied with obvious color change from orange to violet color with the immediate effect. The formation of  $(\text{FZN})_2\text{-Hg}^{2+}$  complex is accompanied with obvious color change from orange to light yellow color (Fig. 2a to 2c). However, the response time of the formazan towards  $\text{Hg}^{2+}$  detection is greater than that for  $\text{Cu}^{2+}$ . Pure FZN dye exhibited strong absorption bands at 254nm and at 474nm with a weak absorption band at 312nm.



Fig. 2a Colorimetric changes of the 3-cyano-1,5-di-p-anisylformazan on addition of 100 equiv. of different aqueous solutions of metal ions



Fig. 2b Colorimetric change of the 3-cyano-1,5-di-p-anisylformazan on addition of 1.0 equiv. of  $\text{Cu}^{2+}$  aqueous solution



Fig. 2c Colorimetric change of the 3-cyano-1,5-di-p-anisylformazan on addition of 100 equiv. of  $\text{Hg}^{2+}$  aqueous solution

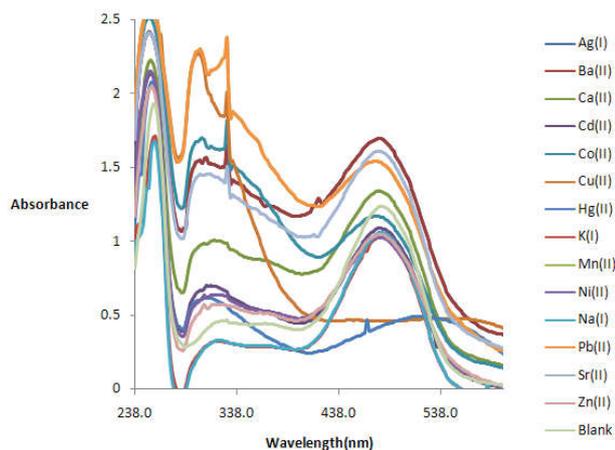


Fig. 3 Change in the UV-visible spectrum of the receptor upon addition of various metal ions

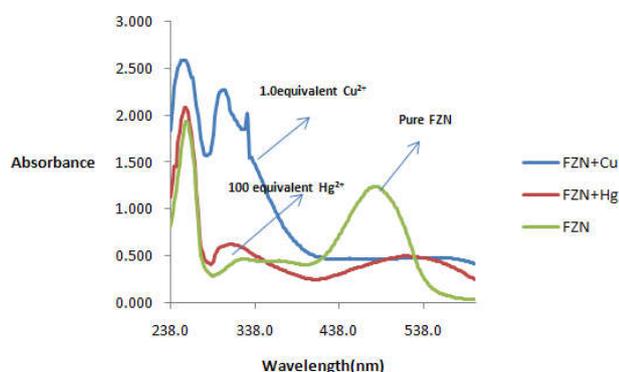


Fig. 4 Change in the UV-visible spectrum of the blank,  $(\text{FZN})_2\text{-Cu}^{2+}$  and  $(\text{FZN})_2\text{-Hg}^{2+}$

To evaluate the sensing behavior of FZN dye toward  $\text{Cu}^{2+}$ , the absorption spectral titration of FZN dye was performed with  $\text{Cu}^{2+}$  in THF+ water (2:3 v/v).

As shown in figure 4, upon addition of  $\text{Cu}^{2+}$  (1.0 equivalent), the intensity of original absorption band at 474 nm and 254 nm progressively decreased. The band at 474 nm broadened thus showing a large scale bathochromic shift whereas the band at 254 nm exhibited a red shift to 244 nm. In addition the weak band occurring at 312 nm became stronger, acquiring absorption maxima at 290 nm along with two isosbestic points at 268 nm and 412 nm (Fig. 5). The appearance of these isosbestic points indicates that only one spectrally distinct  $(\text{FZN})_2\text{-Cu}^{2+}$  (Fig. 6) complex was formed. This is the most probable structure for  $(\text{FZN})_2\text{-Cu}^{2+}$  complex.

As for the other metal ion, only slight variation in the absorbance values have been observed without obvious spectral shift, showing no color switching. It is expected that  $\text{Cu}^{2+}$  owns both atomic radius and large ionic charge, leading to strong and effective ICT transition and correspondingly color switching. The electronic structural difference between the divalent cations with similar atomic radius as that of  $\text{Cu}^{2+}$  is decisive of its tendency to exhibit color switching with FZN. The  $d^9$  electronic configuration favors the participation of d electron in ICT transition leading to color switching. Though the atomic radius of  $\text{Zn}^{2+}$  is almost similar to that of  $\text{Cu}^{2+}$ , the absence of

unpaired d electrons in  $\text{Zn}^{2+}$  prevents ICT transitions responsible for color switching.

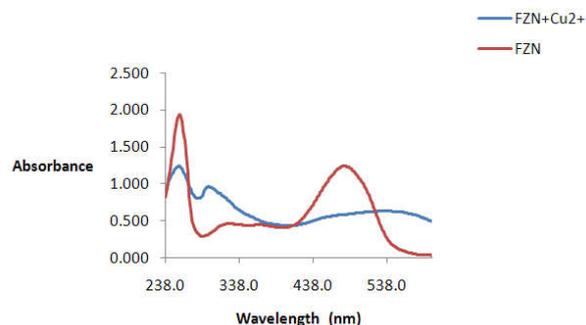


Fig 5 Change in the UV-visible spectrum of the blank,  $(\text{FZN})_2\text{-Cu}^{2+}$

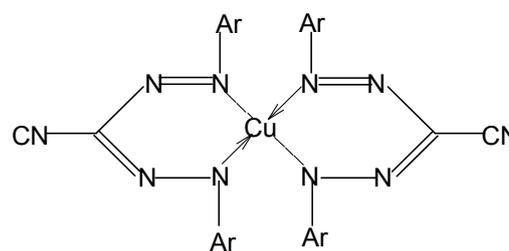


Fig. 6  $(\text{FZN})_2\text{-Cu}^{2+}$  Complex

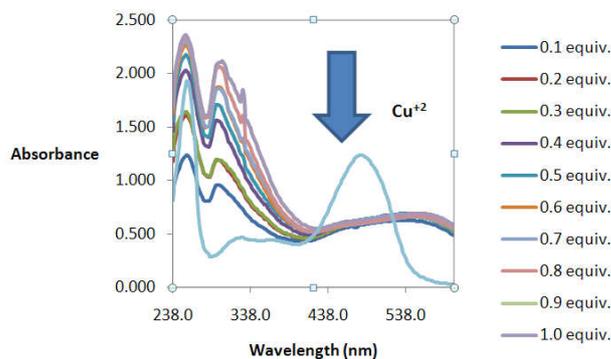


Fig. 7 Change in the UV-visible spectrum of the blank with addition of aqueous  $\text{Cu}^{2+}$  solution

The variations in the absorption spectrum profiles of the compound with addition of various concentration of the aqueous metal ion solutions of  $\text{Cu}^{2+}$ , ranging from 0.1 equivalent to 1.0 equivalent has been depicted in the figure 7.

The proposed stoichiometric complex model of formazan with  $\text{Cu}^{2+}$  has been proposed by a Job's plot in figure 8. This shows a maximum absorbance at 488 nm which corresponds to mole fraction of formazan as 0.33 that is a signature of 2:1 bonding between the receptor and  $\text{Cu}^{2+}$ .

The detection limit for this  $\text{Cu}^{2+}$  ion was found to be  $3.3 \times 10^{-5} \text{ mol L}^{-1}$  and the binding constant K has been found to be  $5.04 \times 10^2$  according to the method reported in the literature.<sup>98,99</sup> Hence easily observable color change in the case of  $\text{Cu}^{2+}$  with the given probe can be used for naked eye detection of  $\text{Cu}^{2+}$  in aqueous media. Similar procedure was followed for  $\text{Hg}^{2+}$  metal ion solution (Fig. 9).

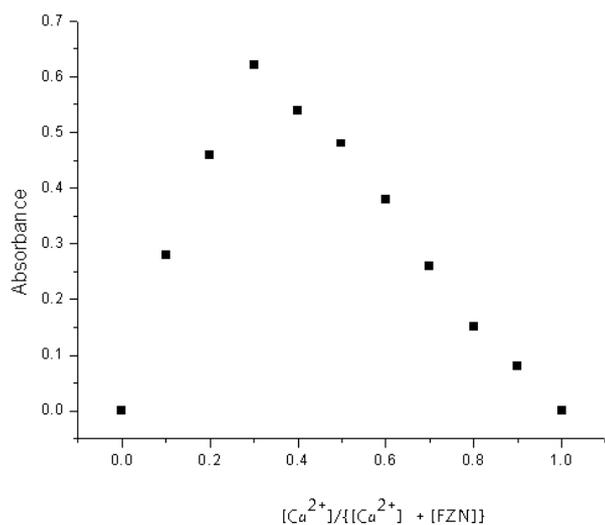


Fig. 8 Job's plot for formation of  $\text{Cu}^{2+}$  and formazan (1:2) complex

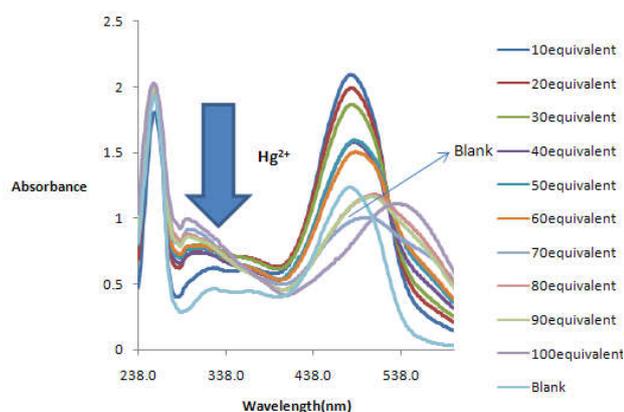


Fig 9 Change in the UV-visible spectrum of the blank with addition of aqueous  $\text{Hg}^{2+}$  solution

The colorimetric studies of 3-cyano-1,5-di-p-tolylformazan, 3-cyano-1,5-di-p-phenylformazan and 3-cyano-1,5-di-p-chloroformazan with  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  revealed almost similar results with slight variation in response time, binding constant and detection limit (table 3 and 4). The small variation is attributed to the difference in electron donating ability of the substituent attached

Table 3 Stoichiometry, detection limit, binding constant of copper complex of 3-cyano-1,5-diarylformazans

Compound	Stoichiometry of Copper Complex	Detection Limit (Mol $\text{L}^{-1}$ )	Binding Constant (K)
3-cyano-1,5-di-p-anisylformazan	2:1	$3.3 \times 10^{-5}$	$5.04 \times 10^2$
3-cyano-1,5-di-p-tolylformazan	2:1	$4.37 \times 10^{-5}$	$4.93 \times 10^2$
3-cyano-1,5-di-p-phenylformazan	2:1	$5.92 \times 10^{-5}$	$3.74 \times 10^2$
3-cyano-1,5-di-p-chlorophenylformazan	2:1	$6.24 \times 10^{-5}$	$2.18 \times 10^2$

Table 4 Stoichiometry, detection limit, binding constant of mercury complex of 3-cyano-1,5-diarylformazans

Compound	Stoichiometry of Mercury Complex	Detection Limit (Mol $\text{L}^{-1}$ )	Binding Constant (K)
3-cyano-1,5-di-p-anisylformazan	2:1	$1.14 \times 10^{-4}$	$1.76 \times 10^2$
3-cyano-1,5-di-p-tolylformazan	2:1	$1.72 \times 10^{-4}$	$1.53 \times 10^2$
3-cyano-1,5-di-p-phenylformazan	2:1	$1.97 \times 10^{-4}$	$1.07 \times 10^2$
3-cyano-1,5-di-p-chlorophenylformazan	2:1	$2.08 \times 10^{-4}$	$7.3 \times 10^1$

### Response Time

Response time is a decisive factor for naked eye colorimetric chemical sensor for in field detection and monitoring. In the present investigation, using FZN as the naked eye colorimetric chemical sensor, it has been found that sensing behavior is observed with immediate effect and sensing signal remain stable.

### Cross Interference between $\text{Cu}^{2+}$ and $\text{Hg}^{2+}$

Achieving high selectivity for the target analyte over a complex background of potentially competitive species is a pre-requisite for a sensor. Since the FZN dye exhibits a colorimetric change for both  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ , it becomes mandatory to examine the extent of interference between  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ . Therefore the ability of the sensor to operate in solution containing 1.0 equivalent of each of  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  was investigated. It was observed that a distinct spectral profile perturbation appeared corresponding to  $\text{Cu}^{2+}$  whereas  $\text{Hg}^{2+}$  failed to respond which clearly proved that our probe possessed selective response to  $\text{Cu}^{2+}$  even in the presence of  $\text{Hg}^{2+}$ .

3-cyano-1,5-di-p-anisylformazan was reacted with  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  separately. Upon incremental addition of  $\text{Hg}^{2+}$  (1 -100 equivalent) to FZN, it was established that  $\text{Hg}^{2+}$  was found to respond in the ratiometric manner at 10 equivalent while the color change could be observed only at 40 equivalent. On the contrary,  $\text{Cu}^{2+}$  starts exhibiting the ratio metric change at 0.1 equivalents and a strong perturbation in the absorption profile at a concentration as low as 1 equivalent was noticed along with the distinct color change (orange to violet). Thereafter the competitive experiment of FZN dye ( $1.29 \times 10^{-6} \text{M}$ ) in the presence of 1 equivalent of each of  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  was carried out and it was found that the probe under consideration retaliated to  $\text{Cu}^{2+}$  even at 1.0 equivalent thereby exhibiting a remarkable colorimetric change and establishing beyond doubt that the FZN dye is a potential naked eye sensor for  $\text{Cu}^{2+}$ . The result indicates that the recognition of  $\text{Cu}^{2+}$  by the FZN dye is not influenced by other co-existing metal ions at 1 equivalent concentration. This finding demonstrates the unique selectivity of FZN dye towards  $\text{Cu}^{2+}$ . The distinctive color change exhibited by FZN dye from orange to violet was attributed to a modulation in intra-molecular charge transfer of the receptor upon effective coordination of  $\text{Cu}^{2+}$  through nitrogen atoms upon its deprotonation

### Molecular Structure of the Receptor

The molecular structure of a receptor is a determining factor of its potential to act as a colorimetric sensor. Both geometric and electronic structures of the receptor under investigation are in compliance with its ability to act as naked eye sensor. The basic design of the formazan moiety makes it appropriate contender to function as an intramolecular charge transfer probe. The formazans possess a co-planar highly conjugated geometry with all atoms barring the  $-CH_3$  group localized in the same plane. Complexation with the metal ion through the nitrogen atoms evolves a large conjugation system that account for large spectral shift in the UV-visible spectral profile paving the way for its use as colorimetric sensor. The potential of the compound as an ICT probe was reflected in terms of big perturbation in the absorption pattern as well as a visual appearance (color change from mustard yellow to light purple) of the compound upon the addition of  $Cu^{2+}$ .

### CONCLUSIONS

The comprehensive spectral shifts in the UV-visible spectrum of the 3-cyano-1,5-diarylformazans were observed when they were subjected to  $Cu^{2+}$  and  $Hg^{2+}$ . The results were more pronounced in the presence of  $Cu^{2+}$  as compared to  $Hg^{2+}$  and hence it is established beyond any doubt that these molecules show excellent selectivity towards  $Cu^{2+}$  even under the influence of other metal ions. The complexation process exhibited in the form of prominent color change (yellow to violet) takes less than 1 minute to accomplish which renders these molecules as a suitable choice to be used for instantaneous detection of  $Cu^{2+}$ . The differently substituted 3-cyano-1,5-diarylformazans showed slight difference in their response towards  $Cu^{2+}$  and 3-cyano-1,5-di-p-anisylformazan showing maximum binding constant is the most stable for the use as colorimetric naked eye sensor.

On the basis of UV-visible spectral data we opined that there is not any pronounced affect of substituents on the ligands and does not affect their use as naked eye colorimetric chemical sensors for the metal ions.

Metal complexation for metal ions with 3-nitro,1,5-diarylformazans is tedious as reported in the literature. The present study has showed that 3-nitro,1,5-diarylformazans cannot be used as naked eye chemical sensors for the metal ions because the reaction between the metal ion and the ligand is not instantaneous and the color change occurs only upon heating for long.

### References

1. Kuhn R and Jerchel D, *Ber. Dtsch. Chem. ges.*, 1941, 74, 949.
2. Mattson AM, Jenson CO and Dutcher RA, *Science*, 1947, 106, 294
3. Pagliacci MC, Spinozzi F, Migliorati G, Fumi G, Smacchia M, Grignani F, Riccardi C and Nicoletti I., *Eur J Cancer*, 1993, 29A, 1573.
4. Pearse AGE, *Histochemistry, Theoretical and Applied*, Churchill Livingstone, 1972.
5. Stoward PJ and Pearse AG, *Histochemistry, Theoretical and Applied*, Edinburgh, Churchill Livingstone., 1991.
6. Hooper W D., *Rev. Pure Appl. Chem.*, 1969, 19, 231.
7. Brault A T and Bissonette V L, *Eastman Kodak.*, 1972, US 3 642 478.
8. Leleental M and Gysling H, *J. Photogr. Sci.*, 1978, 26, 135.
9. Chen W, Wu Y Q, Gu D H and Gan F X, *Mater. Lett.*, 2007, 61, 4181.
10. Baxter A, Bostock S and Greenwood D, 1985, ICI. EP-A 219 232.
11. Sakthivel S, Neppolian B, Shankar MV, Arabindo B, Palanichamy and M, Murugesan V, *Sol Energy Mater Sol Cells.*, 2003, 77, 65.
12. Wan H, Williams R, Doherty P and William DF J, *Materials Science in Medicine* 1994, 5, 154.
13. Tezcan H, Ekmekc G and LeventAksu I M, *Turkish journal of chem.*, 2013, 37, 57.
14. Prodi L. *New J. Chem.* (2005), 29, 20.
15. de Silva A.P., McCaughan B, O.F., Querol M. *Dalton Trans.* (2003), 1902.
16. Anslyn E.V., Angrew, *Chem Int. Ed. Engl.* 40, (2001), 3119.
17. Amendola V., Fabbriizzi L., Mangano C., Pallavicini P., *Acc. Chem. Res.* 34, (2001), 488.
18. Fabbriizzi L., Licchelli M., Pallavicini P., *Acc. Chem. Res.* 32 (1999), 846.
19. Czarnik A.W., *Acc. Chem. Res.* 27 (1994), 302.
20. de Silva A.P., Fox D.B., Huxley A.J.M., Moody T.S., *Coord. Chem. Rev.*, 205 (2000), 41.
21. de Silva A.P., Gunaratne H.Q.N., Gunnlaugsson T., Huxley A.J.M., McLoy C.P., Rademachis J.T., *Rice T.E., Chem. Rev.* 97 (1997), 1515.
22. Wlfbeis O.S., *Fibre Optic Chemical Sensors and Biosensors*; CRC Press: Boca Raton, (1991), Vols. 1 and 2.
23. Orellana G.; Moreno-Bondi, M.C., *Frontier in Chemical Sensors: Novel Principles and Techniques*, Springer; New York, 2005.
24. Callan J.F., Desilva A.P., Magri D.C., *Tetrahedron* 61 (2005), 8551-8588.
25. Martinez-Manez R., Sancenon F., *Chemical Reviews* 103 (2003), 4419-4476.
26. Desilva A.P., Gunaratne, H.Q.N., Gunnlaugsson T.A., Hoxley T.M., McCoy C.P., Rademacher J.T., Rice T.E., *Chemical Reviews* 97 (1997), 1515-1516.
27. Czarnik A.W., *Accounts of Chemical Research*, 27 (1994), 302-308.
28. Kim J.S., Quang D.T., *Chemical Reviews* 107 (2007) 3780-3799.
29. Dickerson T.J., Reed N.N., LaClair J.J., Janda K.D., *Journal of the American Chemical Society*, 126, (2004), 16582-16586.
30. Coskun A., Yilmaz M.D., Akkaya E.U., *Organic Letters* 9 (2007), 607-609.
31. Liu B., Tian H., *Chemical Communications* (2005), 3156-3158.
32. Song K.C., Kim J.S., Park S.M., Chung K.C., Chang S.K., *Organic Letetrs* 8 (2006), 3413-3416.
33. Nolan E.M., Lippard S.J., *Chemical Reviews* 108 (2008), 3443-3480.
34. Waggoner D.J., Bartnikas T.B., and Gitlin J.D., *Neurobiol.* (1999), 221-230.

35. Vulper C., Levinson B., Whitney S., Packman S. and Gitschier J., *Nat. Genet.* (1993), 3(1), 614.
36. Bull P.C., Thomas G.R., Rommens J.M., Forbes J.R. and Cox D., *Nat. Genet* (1993), 5(4), 327-337.
37. Mei Y., Bentley P.A. and Wang W., *Tetrahedron Lett.* (2006), 47, 2447-2449.
38. Chandrasekhar V., Bag P. and Pandey M.D., *Tetrahedron*, (2009), 65, 9876-9883.
39. Liu S.R. and Wu S.P., *Fluoresc.* (2011) 21(4), 1599-1605.
40. Hahn S.H., Tanner M.S., Danke D.M. and Gahl W.A., *Biochem. Mol. Med.* (1995), 54(2), 142-145.
41. Zietz B.P., Vergara J.D. and Dunkelberg H., *Environ. Res.* (2003), 92(2), 129-138.
42. Gao Y. and Ma W., *Optical Materials* (2012), 35,211-216.
43. Tang L., Li F., Liu M. and Nandhakumar R., *Spectrochimica Acta.* (2011), 78, 1168-1172.
44. Beltran O.G., Mena N., Friedrich L.C., Netto-Ferreira J.C., Vargas V., Quina F.H., Nunez M.T. and Cassels B.K., *Tetrahedron Lett.* (2012), 53, 5280-5283.

**How to cite this article:**

Sanjeev Kumar and Rajeev Sharma.2017, Synthesis of 3-Substituted-1, 5-Diarylformazans for Their Use as Naked Eye Chemical Sensor for Detection of CU<sup>2+</sup> AND HG<sup>2+</sup>. *Int J Recent Sci Res.* 8(7), pp. 18172-18178.  
DOI: <http://dx.doi.org/10.24327/ijrsr.2017.0807.0463>

\*\*\*\*\*