

# Spectroscopical view and application of Naphthol Coupled Azo Compounds in complexing and sensing of Fe (II) ions in tap water.

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## ABSTRACT

Four aromatic azo dyes with hydroxyl groups (I-IV) were selected and synthesized by diazo coupling reactions. The relationships between structures of the compounds and their Fe-complexes were done through UV-VIS spectroscopical method. The excellent solubility in green mixture of ethanol-water and simple synthetic process make the compounds potential chromogenic sensor for detecting and complexing Fe<sup>+2</sup> ions presents in tap water without using any catalyst and complicated analytical procedures, which can be visualize even through naked eye. Compounds I-IV could impart proper UV-VIS responses upon addition of Fe (II) metal ions presented 150mg/lit in tap water.

**Keywords:** Azo compounds, Sensors, Naphthols, substituted amines, Fe-complex, tap-water.

## INTRODUCTION

The most studied area under supramolecular chemistry is the recognition of metal ions and neutral species through host-guest interaction theory of non-covalent bonds to form host-guest complexes (Lehn, 1993; 1995). The colorimetric sensing technique provides a favourable and assured detection of medically and environmentally beneficial ions in a very complex state of matter. These sensing agents can be utilized as a detecting kit for onsite testing of harmful or useful species into the environment. On studying the spectroscopical view of the host-guest interaction, researchers has put-forth a theory of increased conjugation or electron density led UV-VIS absorbance of studied molecule results in to red shift of UV-band while when decreased conjugation or electron density the absorbance shifted towards blue wavelength with accordingly changes in colorimetric view which enables molecules to be acts as chromogenic sensors. Taking into accounts of these principles of chromogenic sensing we studied the spectroscopical data of Azo compounds having  $\alpha$  or  $\beta$ - naphthol moiety I-IV and their Fe-complex compounds C-1 to C-4 follows the similar trend of absorption bands in UV spectrum. As per the WHO data, Iron (as Fe<sup>+2</sup>) concentrations of 40  $\mu$ g/litre can be detected by taste in distilled water. In a mineralized water the taste threshold value was 0.12 mg/litre and in well-water, iron concentrations is

below 0.3 mg/litre which is not identifiable, however  $\text{Fe}^{+2}$  content between 0.3–3 mg/litre were acceptable. Concentrations of iron in drinking-water are normally less than 0.3 mg/litre but may be higher in countries where various iron salts are used as coagulating agents in water-treatment plants and where cast iron, steel, and galvanized iron pipes are used for water distribution (National Research Council 1979).

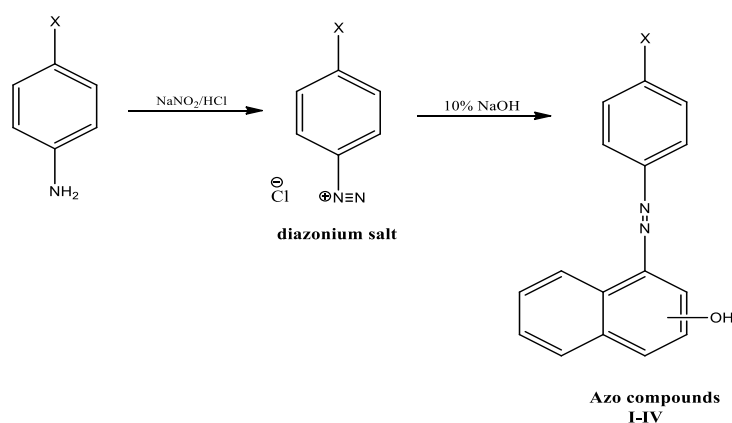
As we know iron is the most abundant d-block element in cellular system which plays an important role in many of the biological processes such as oxygen transportation and DNA synthesis (Que *et al.* (2008), Domaille *et al.* (2008), Haas and Franz, 2009) and Chereddy *et al.* (2013) its deficiency or excess can disturb cellular homeostasis, biochemical metabolism and can cause many diseases like atherosclerosis, cancer and neurological disorder (Fakih *et al.* (2008), Merea *et al.* (2009), Zecca *et al.* (2004), Lipinski (2011), Choi *et al.* (2014 and Vinod kumar *et al.* (2015). An intake of 0.4–1 mg/kg of body weight per day can cause harmful effects on human health the average lethal dose of iron is 200–250 mg/kg of body weight, but death has occurred following the ingestion of doses as low as 40 mg/kg of body weight (WHO 1996). Hence, on this account efforts should be developed to determine the presence of iron content in domestic water. Our study has developed a relationship between all four Azo compounds and their spectroscopical data on binding with Fe (II) ions which can contribute towards the

further preparation of new Azo compounds in the field of Fe (II) recognition in water samples.

Our aim is to explore simply synthesized azo compounds employing easier, one step synthetic route producing expected high yield and utilize them for onsite selective detection of iron in tap water. On this account, we used p-amino toluidine and p-amino acetanalide azo derivatives as a probing unit which can interact differentially with various cations, and apparently become cost effective and sensitive colorimetric probe with high response rates. In the present work, we simply utilized Azo derivatives of substituted amines in complexing with  $\text{Fe}^{+2}$  cation over other examined cations dissolved in tap water. The details study about their spectroscopical characterisation before and after formation of Fe-Complex is investigated and discussed thoroughly.

## MATERIAL METHODS

The Azo compounds **I-IV** was synthesized through given scheme by following literature in which it was reported (Xu 2017). Performed compounds **I-IV** was identified by, FT-IR, (C, H, N) analysis and UV-Vis spectral mechanisms which has been exactly in tune with the reported work. An aqueous- Ethanol solutions were performed to make I-IV soluble and incorporate them for studying interaction of the metal ions Fe (II) in tap water.



**Scheme for synthesis of Azo compounds I-IV**

| Molecular representations | X-substituent on amines | Coupling Phenols   |
|---------------------------|-------------------------|--------------------|
| I                         | -CH <sub>3</sub>        | $\alpha$ -naphthol |
| II                        | -CH <sub>3</sub>        | $\beta$ -naphthol  |
| III                       | -NHCOCH <sub>3</sub>    | $\beta$ -naphthol  |
| IV                        | -NHCOCH <sub>3</sub>    | $\alpha$ -naphthol |

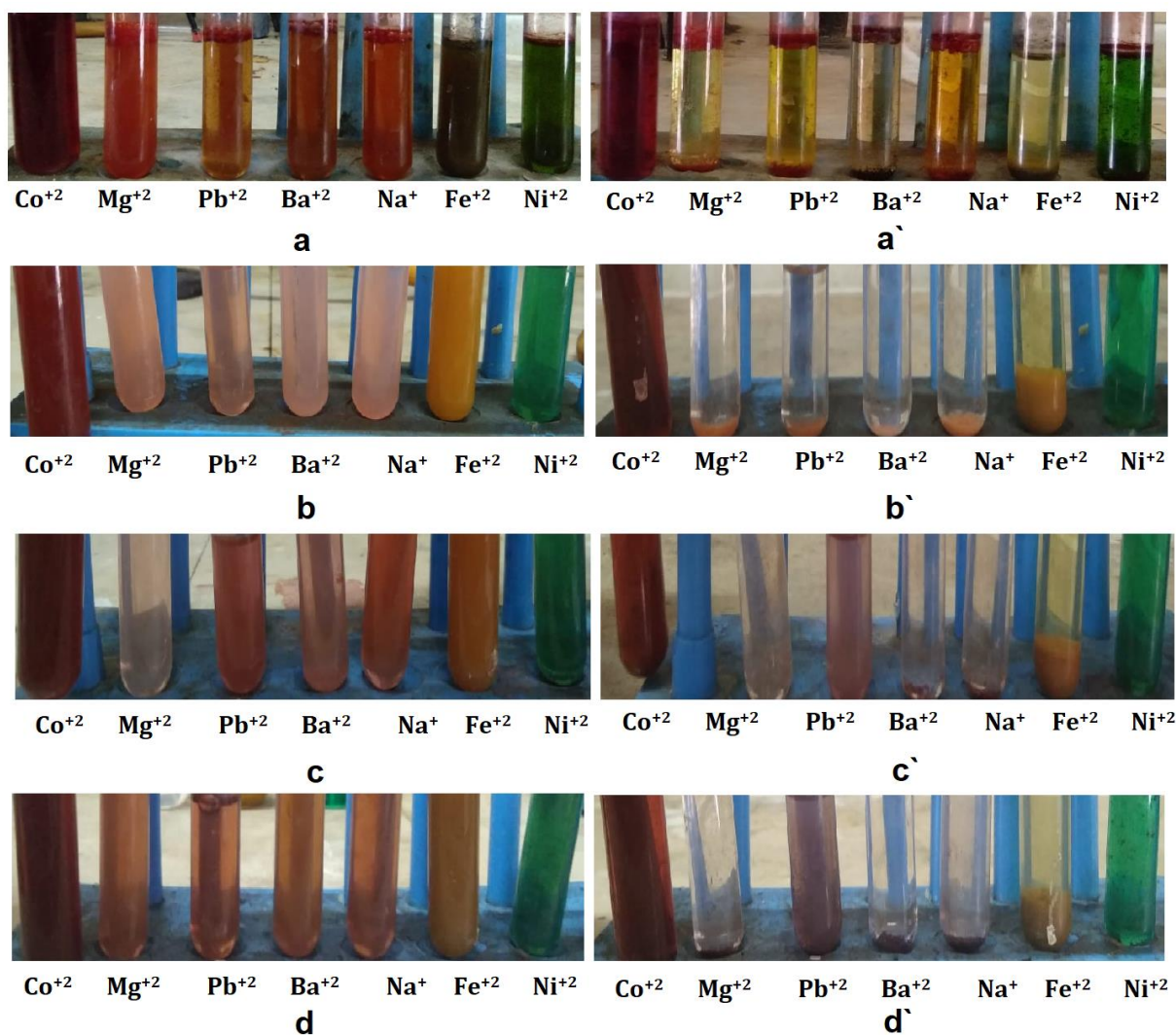
The solid complexes is formed by immediate interaction of the 1M aqueous ethanolic solution of **I-IV** and the 0.01 Fe(II) ions solution dissolved in water (tap water) (which is 150 mg/lit) at perfect pH. The colour of the solid product is visualized at Zero time (T=0) and after 12 hrs (T=12).

## RESULTS & DISCUSSION

On immediate addition of Fe (II) ion solution in **I-IV** we observe at t=0 the change in colour of solution from light yellow to dirty yellow while after T=12 hrs there was a formation of dirty to blackish yellow coloured solid compound (C-1, C-2, C-3 and C-4) respectively (shown in Fig-1). The UV-VIS absorbance data for **I-IV** and their respective Fe-complexes are shown in fig-2

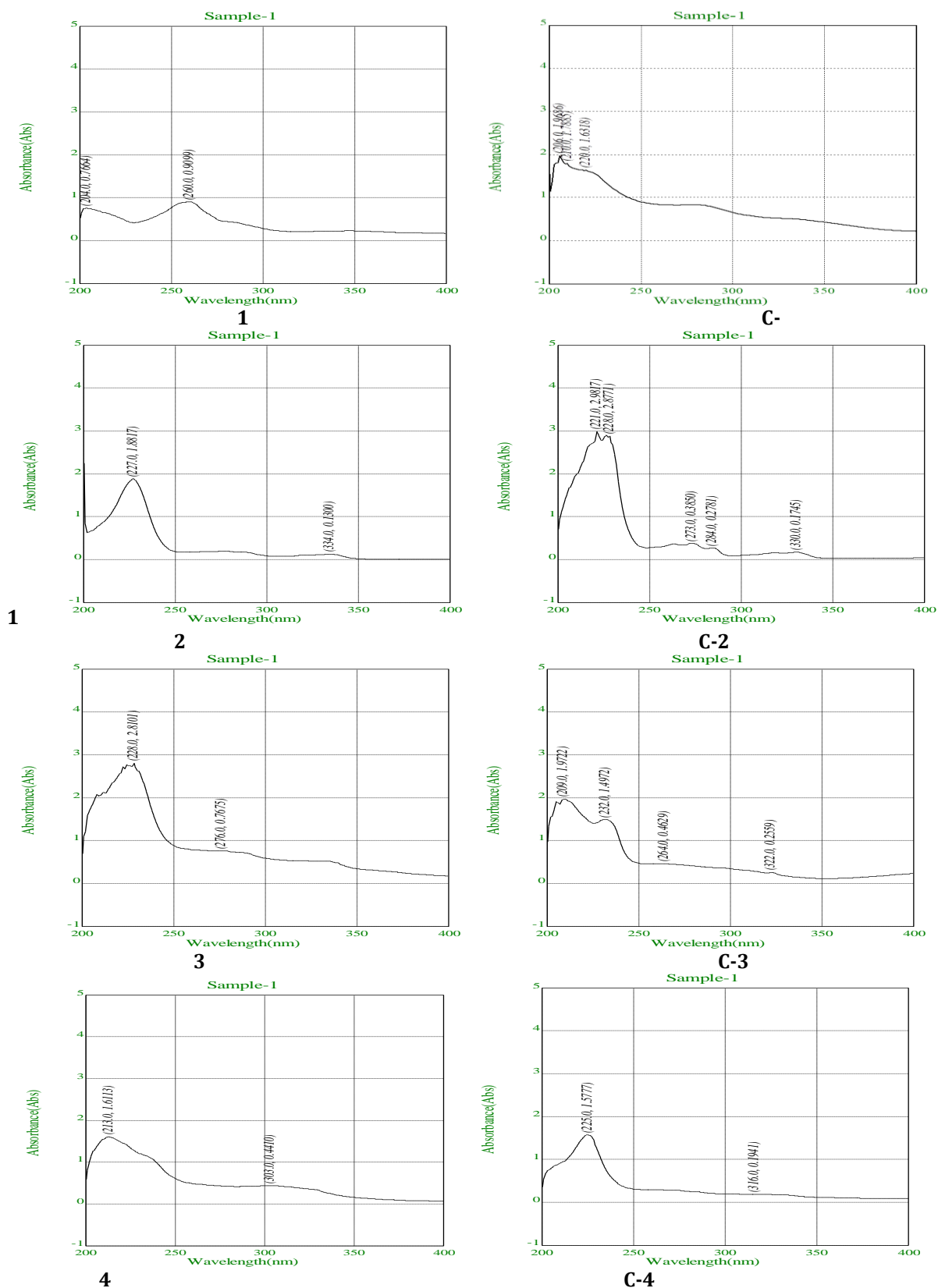
### The Spectroscopical view for 1-4 and complexes:

The UV spectrum of the free Azo compounds **I-IV** (given in Table-1) shows a strong bands at 204 nm , 227nm ,228nm and 213nm respectively, which is attributed to  $\pi \rightarrow \pi^*$  transition. Another bands were also observed at 260,334,276 and 303 nm due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions respectively (Wolfgang *et al.* (2003) and Emel Y and Hamit B (2002). These values for  $\pi \rightarrow \pi^*$  transition do not change more between free compounds and their complexes except value for  $n \rightarrow \pi^*$  (260 and 334 nm) which shifted to lower wavelength for C-1 and C-2, and (276 and 303nm) shifted to higher wavelength for C-3 and C-4 complexes this mean corporation of the pair of electrons of azo group in binding with metal.



**Fig-1** -The photographical view

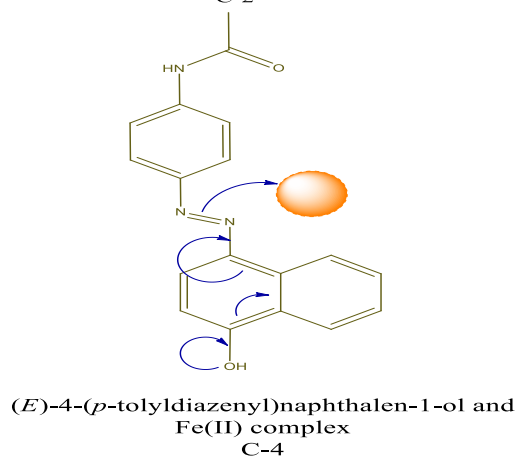
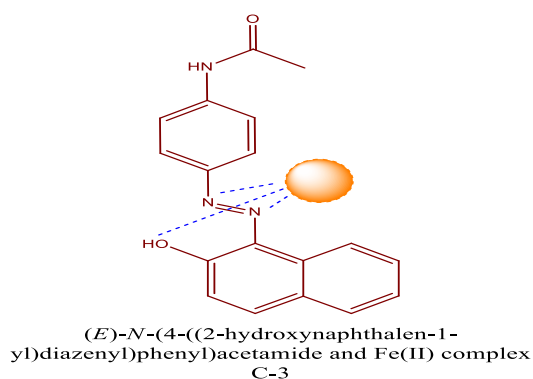
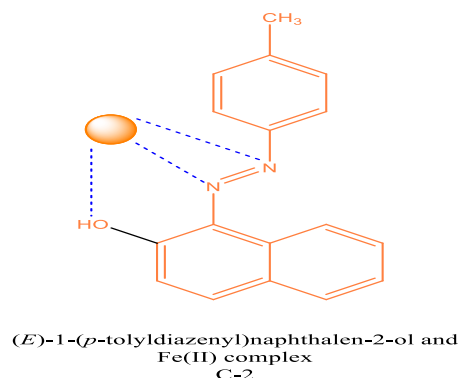
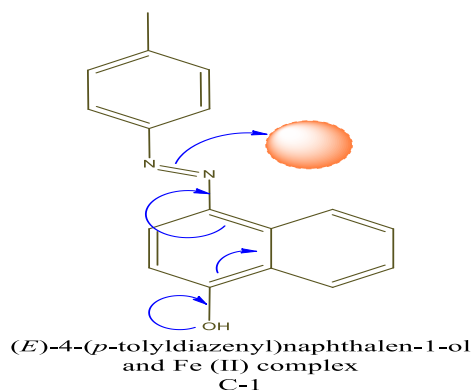
(i) images **a, b, c, d** and **a', b', c', d'** - for addition of **I-IV** in  $\text{Co}^{+2}, \text{Mg}^{+2}, \text{Pb}^{+2}, \text{Ba}^{+2}, \text{Na}^{+}, \text{Fe}^{+2}, \text{Ni}^{+2}$  solution at time =0 and time=12 hrs respectively.



**Fig-2** -A UV-VIS spectra i) 1, 2, 3 and 4 for azo compounds I-IV in Free State  
 ii) C-1, C-2, C-3 and C-4 for Fe-complex of I-IV

**Table-1:** Showing UV bands for I-IV and new bands for their Fe-complexes due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition

| Azo compounds | UV absorbance in nm     |                                    |                       |                                  |
|---------------|-------------------------|------------------------------------|-----------------------|----------------------------------|
|               | $\pi \rightarrow \pi^*$ | Fe-complex $\pi \rightarrow \pi^*$ | $n \rightarrow \pi^*$ | Fe-complex $n \rightarrow \pi^*$ |
| I             | 204                     | 206                                | 260                   | 220                              |
| II            | 227                     | 228                                | 334                   | 330,228,273                      |
| III           | 228                     | 209,232                            | 276                   | 322,264                          |
| IV            | 213                     | 225                                | 303                   | 316                              |



### Mechanistic Pathways for Fe-complexation

We observed an enhancement in the absorption peaks of azo compounds upon addition of  $\text{Fe}^{+2}$  solution with formation of solid product along with simultaneous change in color from light yellow to yellowish brown. This suggests that, the azo compounds III and IV can serve as a potential candidate for "naked eye"  $\text{Fe}^{+2}$  detectors and led to form a complex compound. While there was a decrease of absorption peaks in azo complex C-1 and C-2 after addition of  $\text{Fe}^{+2}$  solution which also results into formation of blackish yellow and dark yellow solid products respectively. In  $\alpha$ -naphthol coupled azo compounds there was an appearance of split of bands in C-2 and C-3, the reason is probably that the interaction between  $\text{Fe}^{+2}$  ion and the detector II and III, weakens the conjugated properties of the molecule or may be enlarging of the conjugation length of the systems (Wang *et al.* 2013).

For  $\beta$ -Naphthol coupled azo compounds complex C-1 shows a blue shift of 40nm from 260nm to 220nm due to increase in HOMO- LUMO gap<sup>16</sup>, while the complex C-4 shows a red shift by 13nm from 303nm to 316nm due to longer conjugation because of presence of acetamide group on *p*-position.

For C-2 and C-3 which are  $\alpha$ -naphthol coupled azo compound complex show splitting in there UV absorbance bands due to shortening of conjugation in both of the complex and also they exhibit blue shift in  $n \rightarrow \pi^*$  by 4nm (i.e. 334 to 330 nm) and 12nm (276 to 264nm) respectively due to engaging of -OH lone pairs in binding of  $\text{Fe}^{+2}$  ion during complexation (Ogawa *et al.* (2009) and Manas FS and Chen LX (2000) which results into decrease in electron density and HOMO-LUMO gap. However, there is a red shift in absorption band for  $\pi \rightarrow$

$\pi^*$  in C-2 and C-3 by 45 nm (from 228 to 273 nm) and for  $n \rightarrow \pi^*$  by 46 nm (from 276 to 322 nm) respectively, this is probably due to donating Inductive effects of  $-\text{CH}_3$  and donating resonance effect of acetamide group on para to  $-\text{N}=\text{N}-$  linkage. Here it is also assumed that the red shift appears in  $n \rightarrow \pi^*$  transitions in C-3 rather than  $\pi \rightarrow \pi^*$  transitions in C-2, this may be due to involvement of acetamide group nitrogen lone pair in delocalization inside the benzene ring which is not possible in C-2 as there is a presence of  $-\text{CH}_3$  group.

## CONCLUSION

The azo dyes were synthesized by simple synthetic process with high yield and preparing its aqueous ethanolic solution we investigated their binding application for  $\text{Fe}^{+2}$  ions in tap-water, the investigation of relationship between structures of all four reported azo compounds and spectroscopic properties were concluded about compounds I-IV which could afford proper UV-VIS responses upon addition of  $\text{Fe}(\text{II})$  metal ions presented as 150mg/lit in tap water. Excellent water-ethanol solubility and simple synthetic process make all four applicable for sensing  $\text{Fe}(\text{II})$  in domestic water. These results may contribute to the development of a new azo compounds for the sequential recognition of  $\text{Fe}(\text{II})$  in water samples below 150 mg/lit concentration.

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