Electronic Supplementary Information

Salicylazine activated plasmonic Silver Nanoprisms for deciphering Fe(II) & Fe(III) from their aqueous solutions

Deovrat Singh,[a] Raksha Singh,[a] Abhay Kumar,[a] Anurag Kumar Singh,[a] Minu Yadav,[a] and K.K.Upadhyay [a*]

* Corresponding author

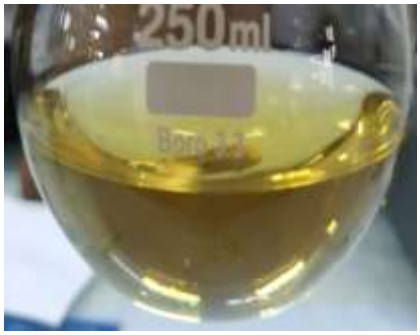
[a] Department of Chemistry (Centre of Advanced Study), Institute of Science, Banaras Hindu University, Varanasi 221005, India
E-mail: drkaushalbhu@yahoo.co.in

New Journal of Chemistry

Table of Contents

(a)

(b)



(c)

(d)

Figure S1. Photographs showing: (a) Synthesized AgNPs , (b) Blank run in absence of $AgNO_3$, (c) Blank run in absence of Schiff base (Salicyl azine) , (d) Blank run in absence of NaOH .

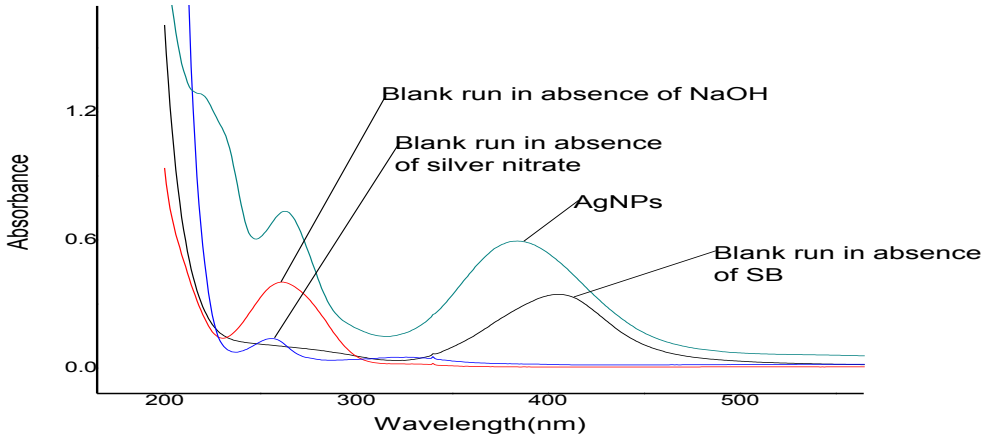


Figure S2: UV-Vis Spectra of AgNPs and various controlled preparations

Nanoparticle Volume, Mass and Concentration

Volume of Silver Nanoparticle = 2831.765 nm^3 (approx.).

Concentration of Silver Nanoparticle:

$N = M_C / m$

where M_C is the mass concentration of the measured element and m is the mass of an individual nanoparticle. If the total mass concentration is expressed in units of g/mL, and the particle mass has units of g/particle, the calculated concentration has units of particles/mL

In our experiment we have:

Salicylaldehyde Azine(w1) = 240 g C1= 240/100 = 2.40 g/ml

Silver Nitrate(w2) = 169.87 g C2 = 169.87/100 = 1.69 g/ml

NaOH(w3) = 40 g C3 = 40/100 = 0.40 g/ml

Water(w4) = 18 g C4 = 18/100 = 0.18 g/ml

Chloroform(w5) = 119.38 g C5 = =119.38/100 = 1.19 g/ml

M_C = C1+C2+C3+C4+C5 = (2.40+1.69+0.40+0.18+1.19) g/ml = 5.86 g/ml

For a hexagonal nanoparticles, $V = 3 \times 1.73 \times s^2 \times h / 2$

$V_1 = 3 \times 1.73 \times 19 \times 19 \times 3 / 2 = 2810.4\ nm^3 = 2.810 \times 10^{-18}$ ml

$V_2 = 3 \times 1.73 \times 17 \times 17 \times 0.8 / 2 = 599.96\ nm^3 = 0.6 \times 10^{-18}$ ml

$V_3 = 3 \times 1.73 \times 18 \times 18 \times 4.5 / 2 = 3783.51\ nm^3 = 3.78 \times 10^{-18}$ ml

$V_4 = 3 \times 1.73 \times 21 \times 21 \times 3.6 / 2 = 4119.82\ nm^3 = 4.12 \times 10^{-18}$ ml

V_{mean}= (2.810 + 0.6 + 3.78 + 4.12) × 10^{-18} / 4 = 2.83 × 10^{-18} ml

$m_{individual}$ = densiity$_{Ag}$ × V_{mean} = 10.5 g/ml × 2.83 × 10^{-18} ml = 2.97 × 10^{-17} g/particle

Number Concentration of Nanoparticle:

N = M_c / $m_{individual}$ = 5.86 g/ml / 2.97 × 10^{-17} g/particle

= 1.97 × 10^{17} particles/ml (approx..)

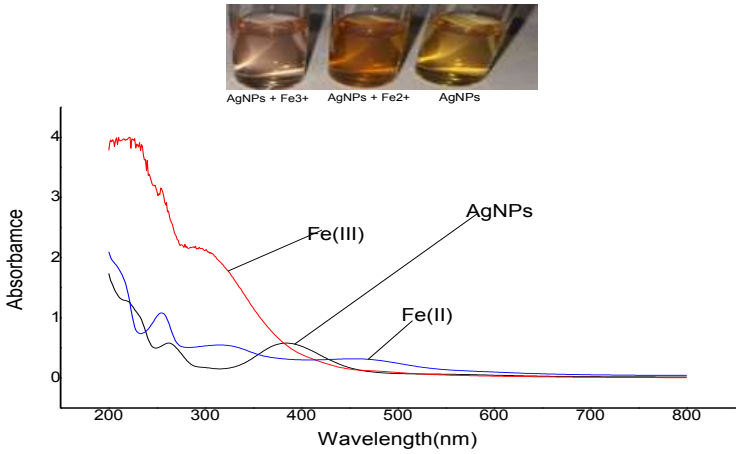
Nanoparticle Concentration in Molar Concentration:

The particle molarity is calculated as

M = N/6.023 × 10^{23}

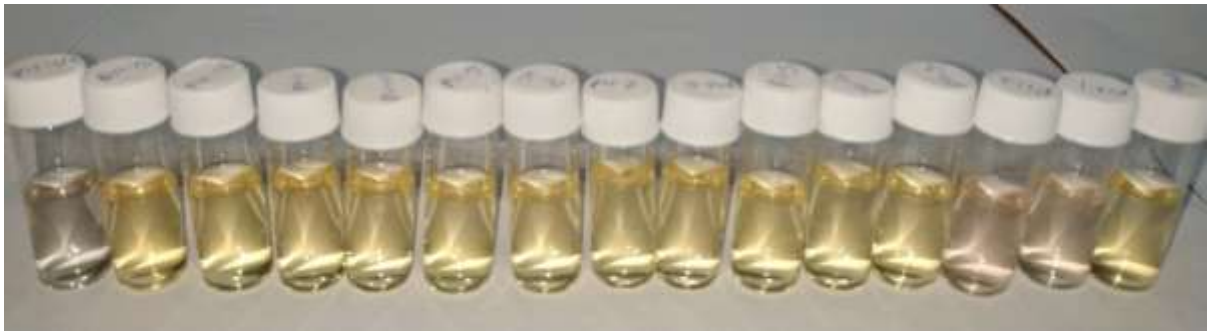
M = 1.97 × 10^{17} / 6.023 × 10^{23}

= 327 nM



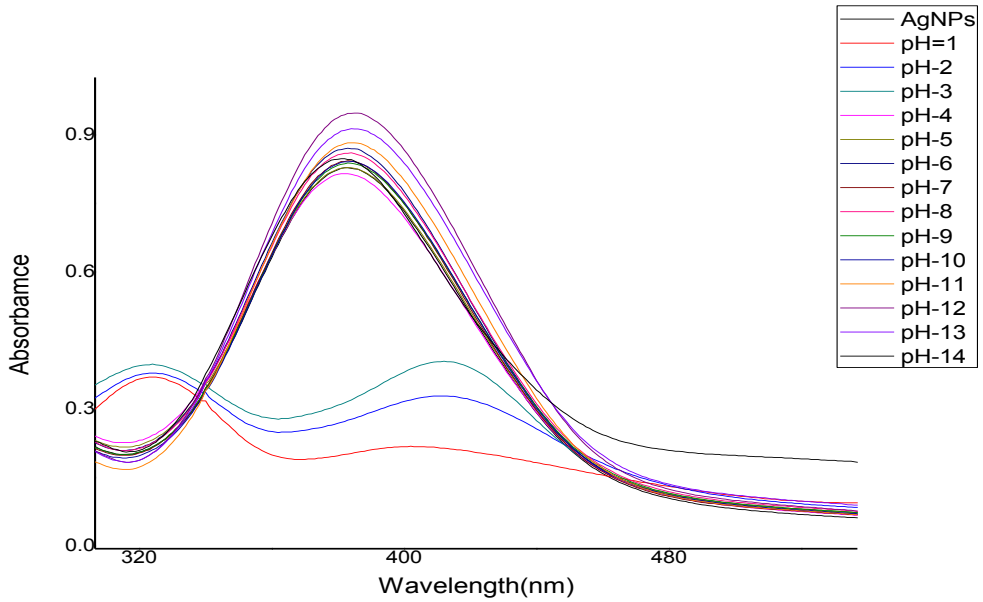
Visual Responses: AgNPs and their interaction with Fe^{2+} and Fe^{3+} along with their corresponding UV-vis spectra.

Figure.S3



14 13 12 11 10 9 8 7 6 5 4 3 2 1 AgNPs

(a)

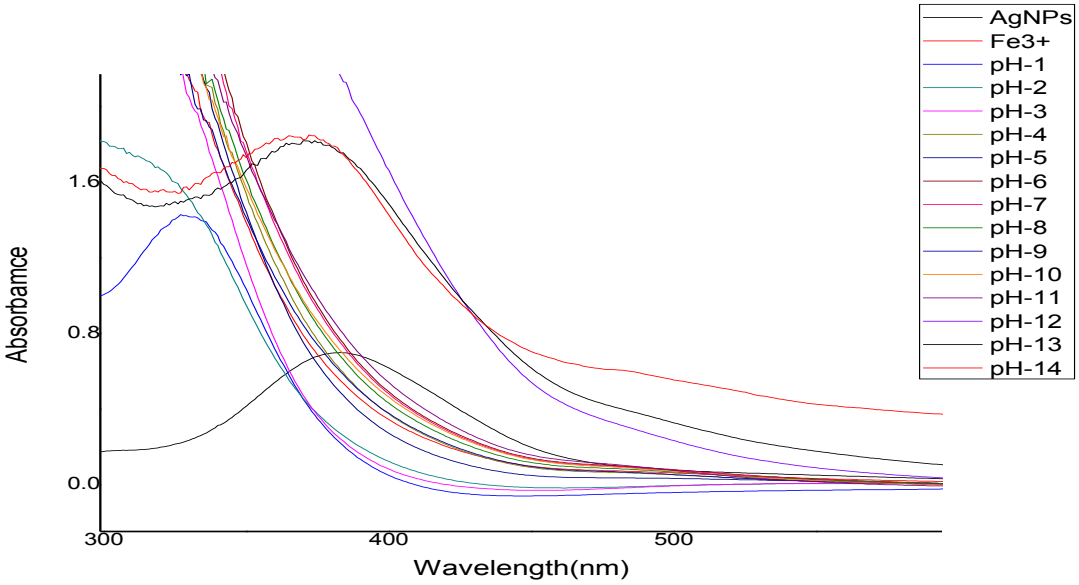


(b)

Figure S4 : Effect of pH variation (1-14) on AgNPs :(a) Visual changes in AgNPs (b) Corresponding UV-Visible spectra of AgNPs.

14 13 12 11 10 9 8 7 6 5 4 3 2 1 Fe3+ AgNPs

(a)

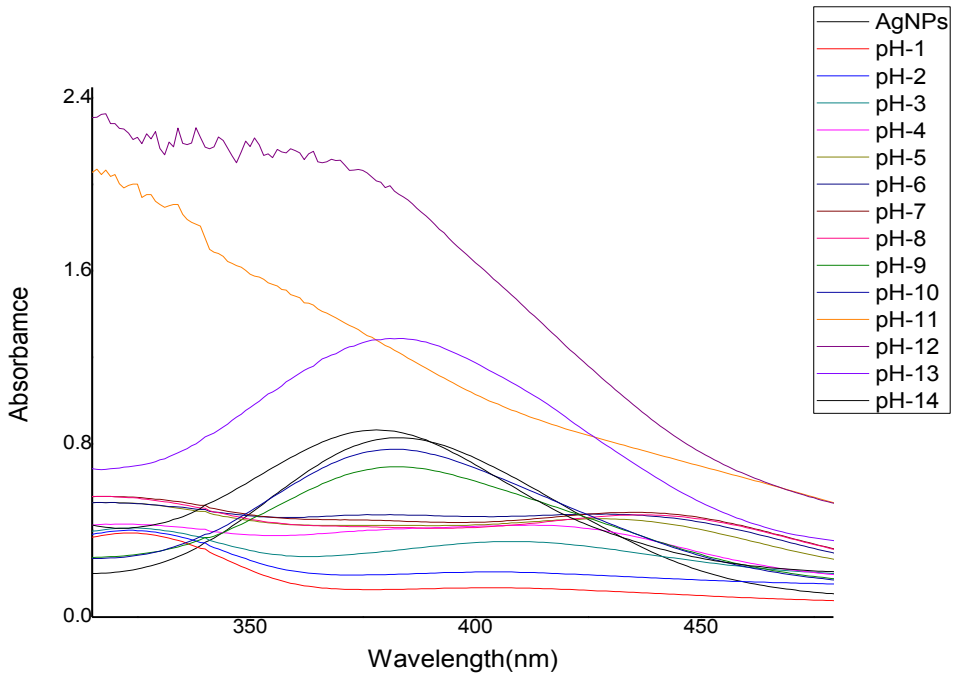


(b)

Figure S5: pH studies : (a) Sensing of Fe3+ with AgNPs ,(b) Corresponding UV-Visible Spectra.

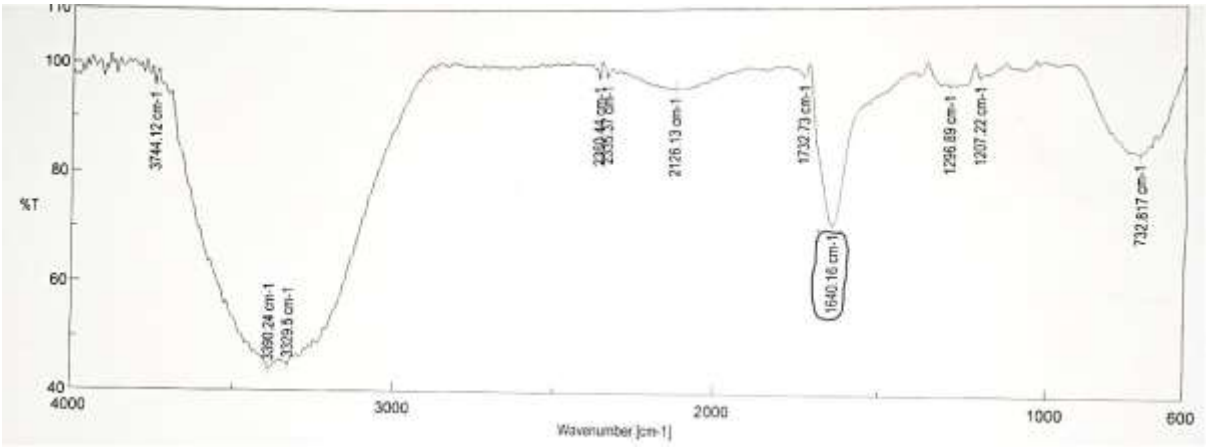
AgNPs Fe2+ 1 2 3 4 5 6 7 8 9 10 11 12 13 14

(a)

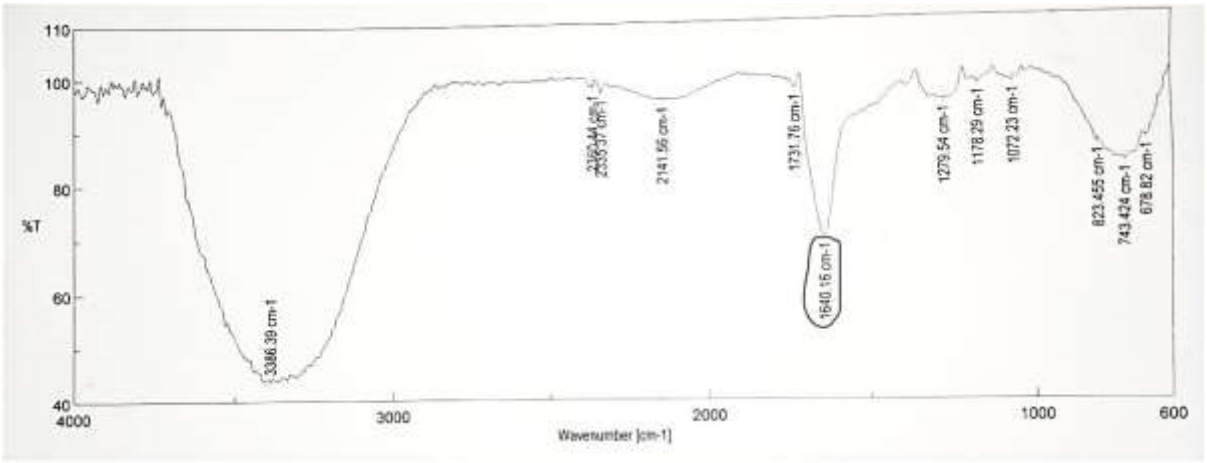


(b)

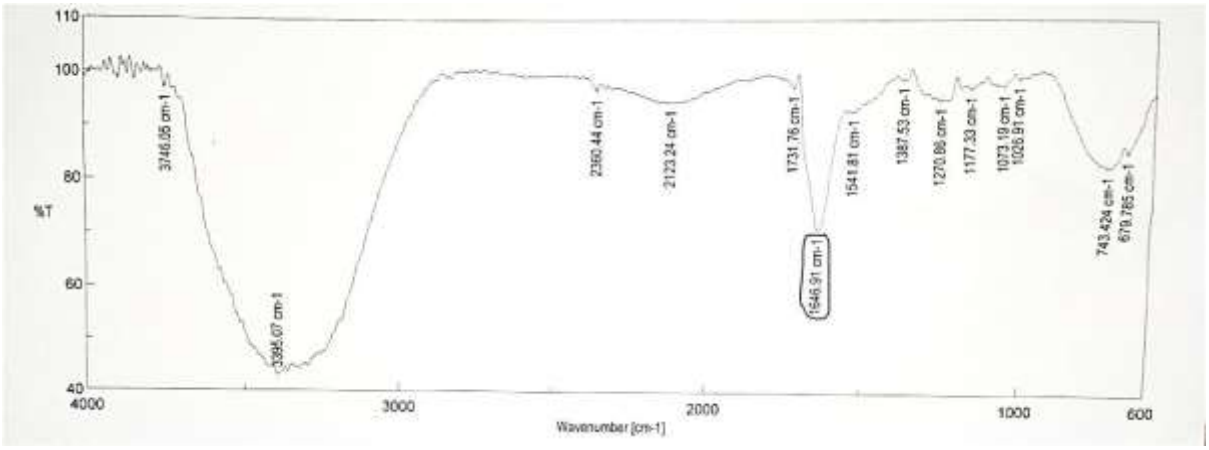
Figure S6 : pH studies : (a) Sensing of Fe^{2+} with AgNPs (b) Corresponding UV-Vis Spectra.



(a)

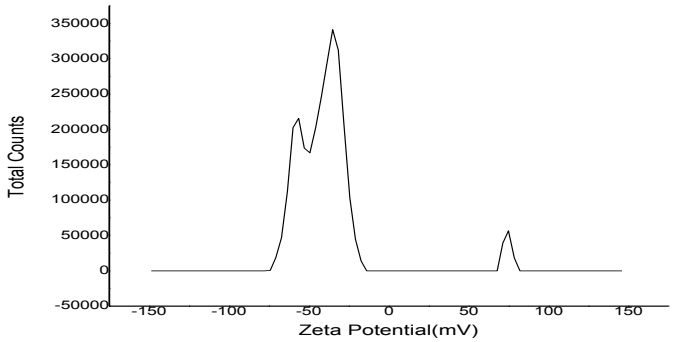


(b)

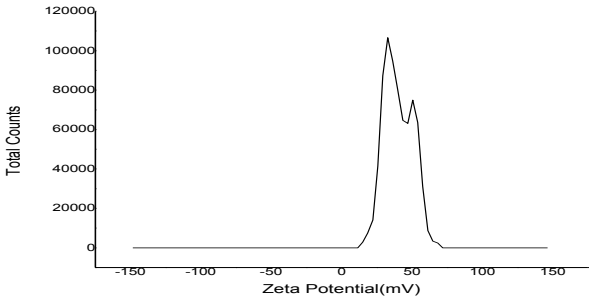


(c)

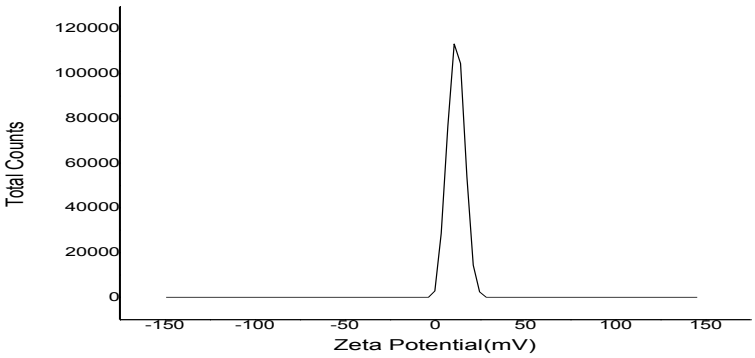
Figure S7 : Showing (a) FT-IR of AgNPs ; (b) FT-IR for the sensing of Fe^{2+} with AgNPs ; (c) FT-IR for the sensing of Fe^{3+} with AgNPs.



(a)

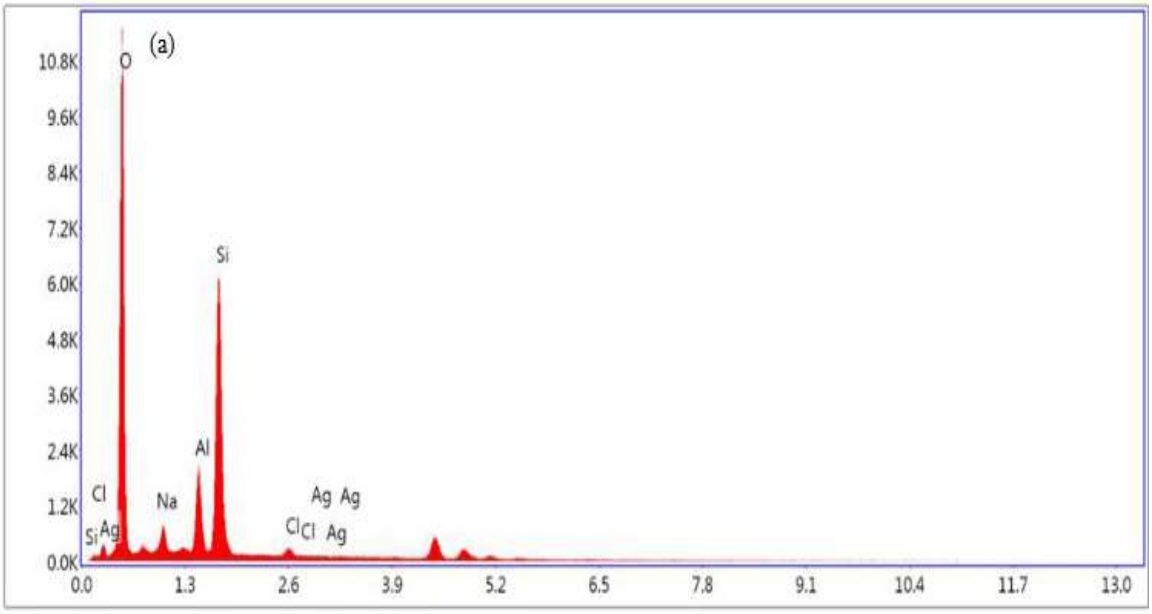


(b)

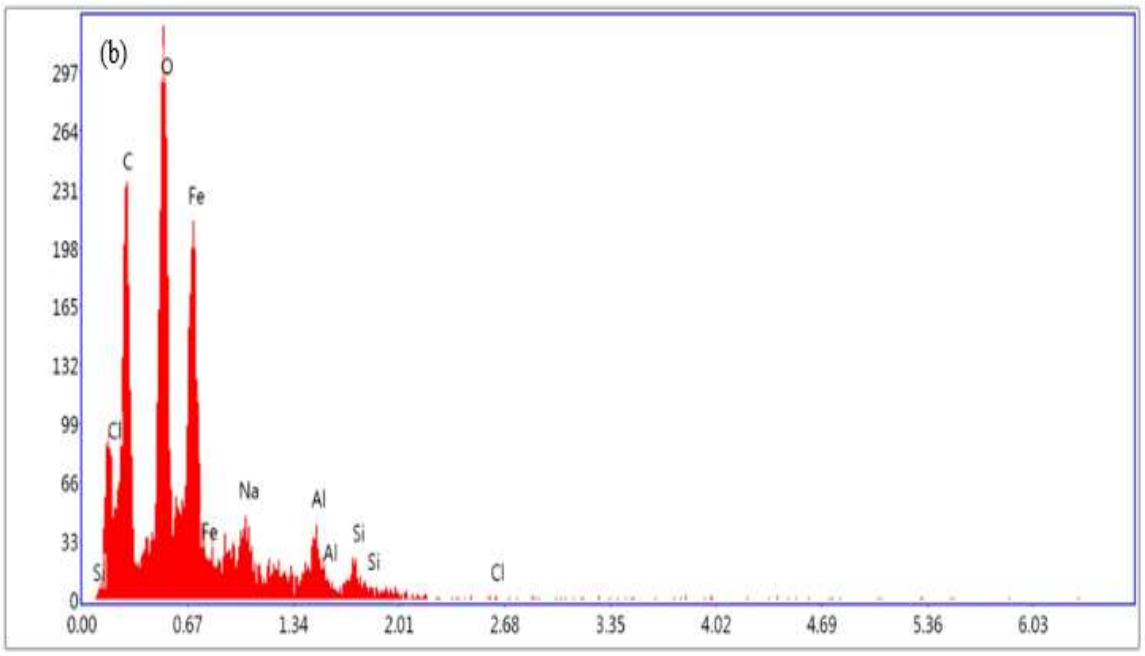


(c)

Fig S8: Zeta Potential values of (a) AgNP ;(b) Interaction of AgNPs with Fe^{3+} ; (c) Interaction of AgNPs with Fe^{2+}.

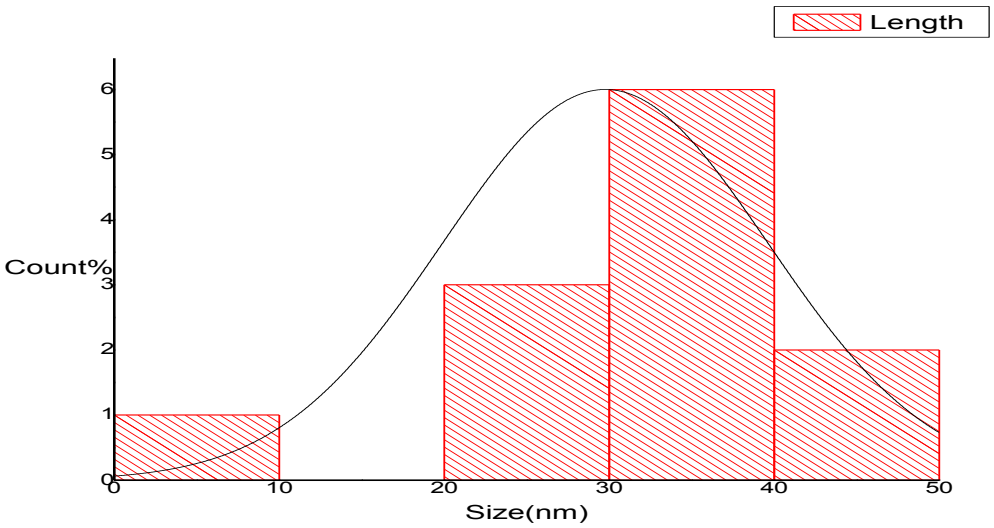


(a)

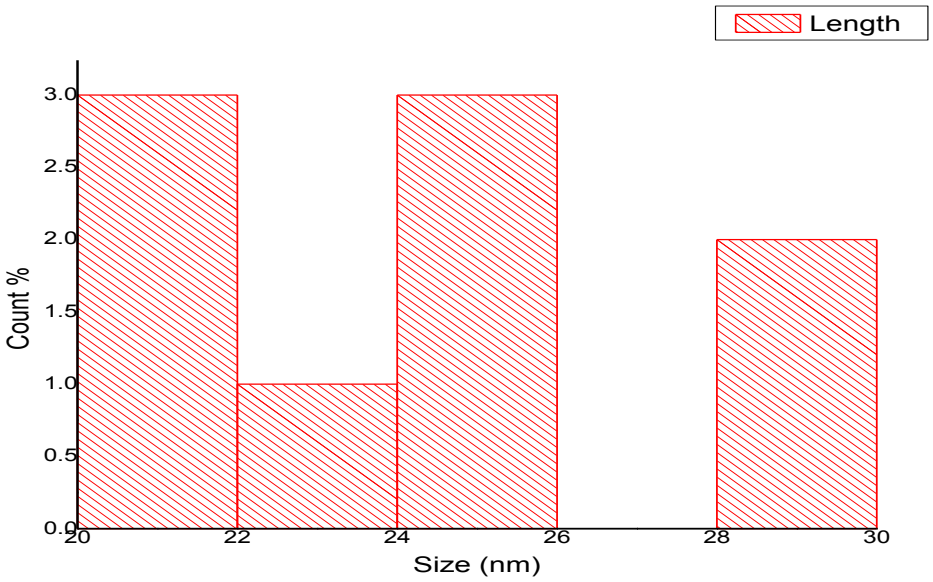


(b)

Figure S9 Showing EDX study of (a) AgNPs ; (b) One of its sensing part with Fe^{3+}.



(a)



(b)

Figure S10: (a) Histogram Curve showing distribution of AgNPs, (b) Histogram Curve showing size distribution of AgNPs after interaction with Fe(II).

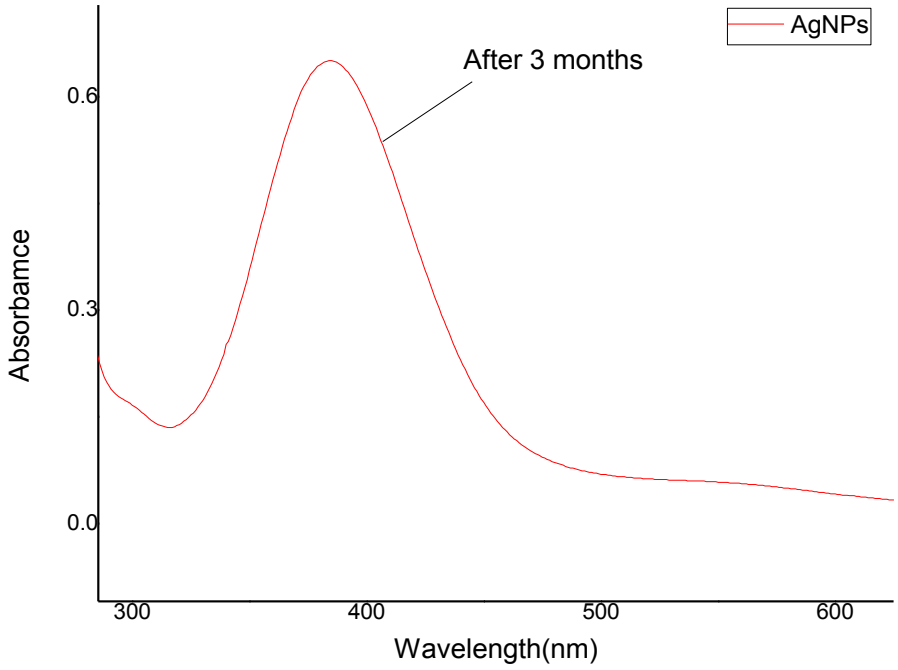
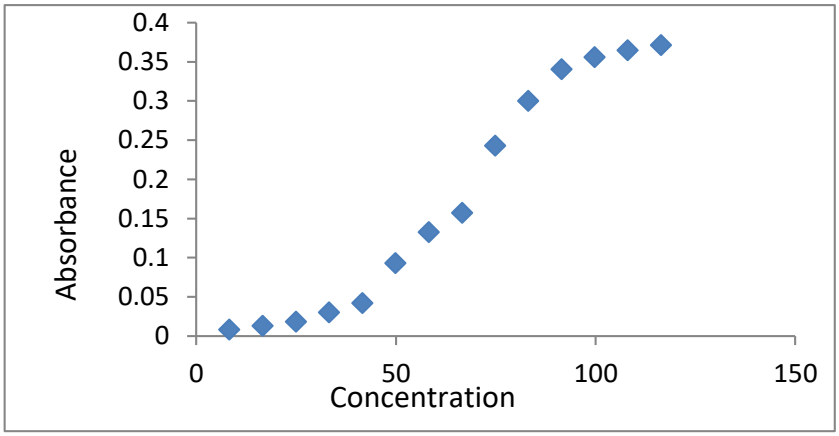


Figure S11: SPR band of AgNPs after 3 months of its preparation.



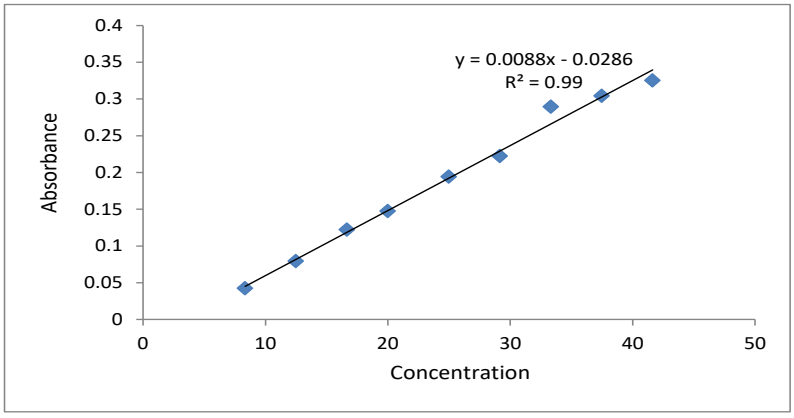
LOB = mean $_{blank}$ + 1.645 sigma $_{blank}$

LOD = LOB + 1.645 sigma $_{low\ concentration\ sample}$

LOD of Fe^{3+}= 0.9 nM.

(Biomolecular Detection and Quantification ,**12**, June 2017, Pages **1-6**)

(K. Besar , J. Dailey , X. Zhao , & H.E. Katz , *J. of Mat. Chemistry C,2017*, **5(26)** , 6506–6511)



LOD = 3 × Standard Deviaton of response / Slope of calibration curve

LOD of Fe^{2+} = 3.47 nM (approx.)

(O.B. da Silva and Sergio A. S. Machado , *Anal. Methods*, 2012,**4**, 2348-2354)

Figure S12

Figure S13 : Comparison of sensing performance towards Fe^{3+} and Fe^{2+} (in terms of LOD) of our AgNPs with others

Analytes	Detection Limit	Refrences
Fe^{2+} and Fe^{3+}	3.47 nM and 0.9 nM	Present Study
Fe^{2+} and Fe^{3+}	1 μM and 5 μM	[1]
Fe^{2+}	5×10^{-5} M	[2]
Fe^{3+}	17 nM	[3]
Fe^{3+}	10^{-3} M	[4]
Fe^{3+}	1.29 μM	[5]
Fe^{3+}	0.0894 nM	[6]

1. K. Dayanidhi and N. Sheik Eusuff , *New J. Chem.*, 2021,**45**, 9936-9943.

2. X. Chen, X. Cheng and J. Justin Gooding, *Analyst*, 2012,**137,** 2338-2343.

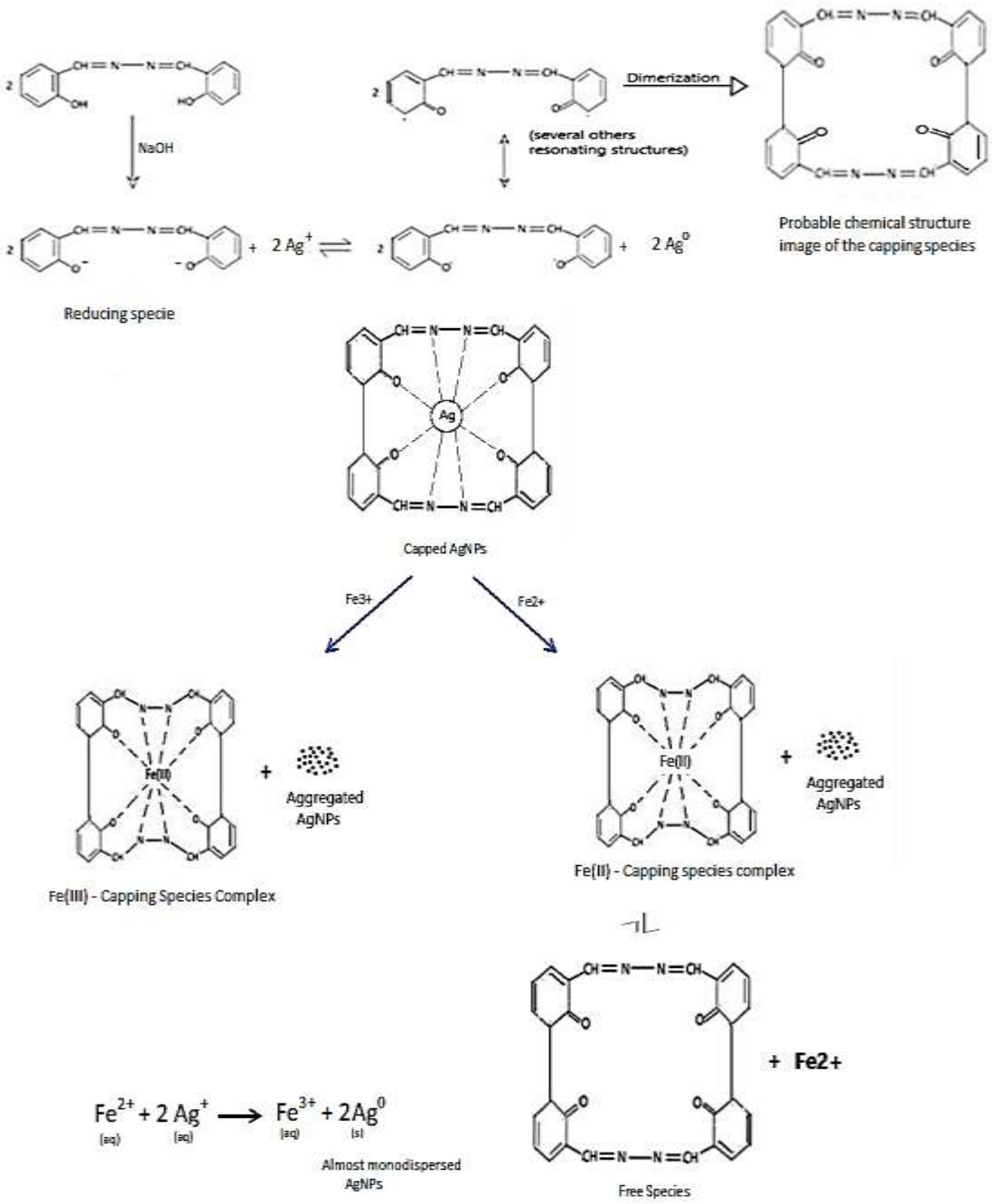
3. M. S. Coutinho, E. Latocheski, J. M. Neri, A. C. O. Neves, J. B. Domingos, L. N. Cavalcanti, L. H. S. Gasparotto, E. P. Moraes and F. G. Menezes, *RSC Adv.*, 2019,**9**, 30007-30011.

4. S. K. Chandraker, M. K. Ghosh, M. Lal, T. K. Ghorai and R. Shukla , *New J. Chem.*, 2019,**43**, 18175-18183.

5. S. Bothra, J. N. Solanki, S. Sahoo, *Sensors and Actuators B Chemical* ,2013, **188**:937-943.

6. R. Azimpanah, Z. Solati , M. Hashemi, *IET Nanobiotechnology,2018,* **12(5)** , 673–677.

Figure S14 : Probable Mechanism for the formation of Silver Nanoparticles and their sensing action towards Fe^{3+} /Fe^{2+}



L. Li, F. Hu, D. Xu, S. Shen and Q. Wang, *Chem. Commun*., 2012, **48**, 4728–4730.

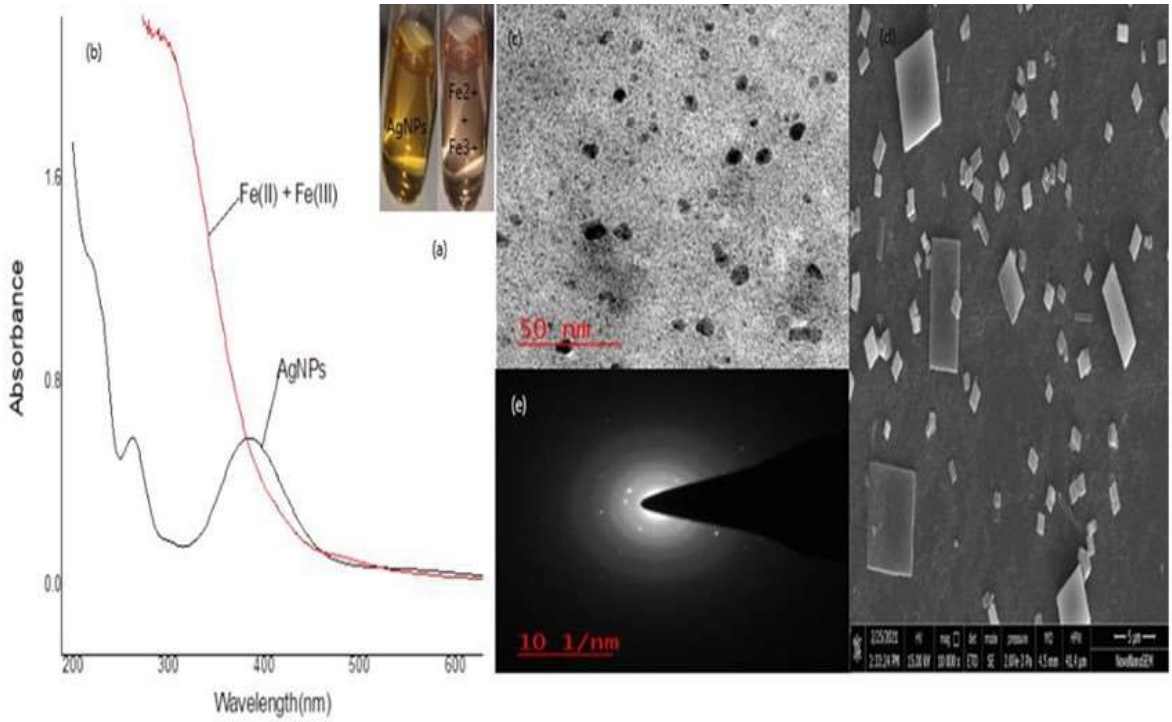


Figure S15 : Showing (a) Visual changes in AgNPs upon addition of a mixture of Fe^{2+} & Fe^{3+} (b) Corresponding UV- Vis spectra (c) HRTEM (d) FESEM (e) SAED .

Studies on performance of AgNPs towards a few real samples

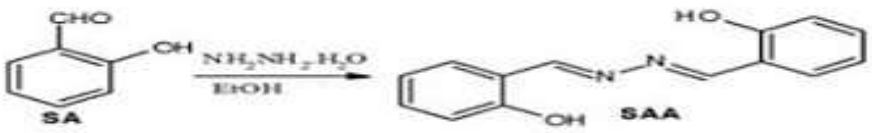
Two sets of real samples were studied :

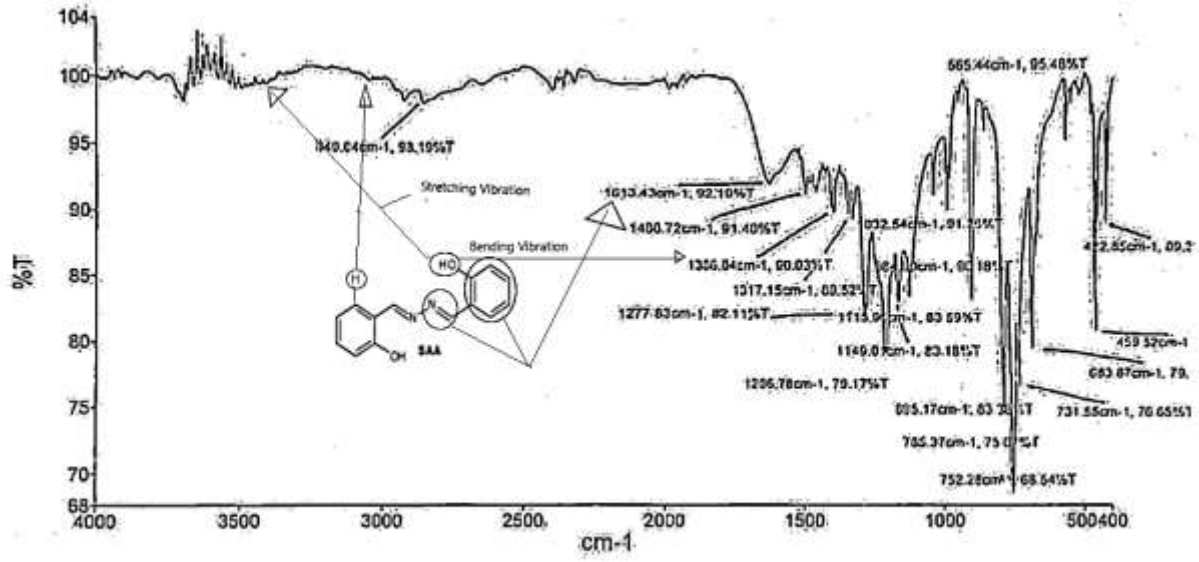
1. Water samples viz. Millipore, Tap and Pond water : In three separate vials of 4mL capacity ,2mL water was taken of each type. 1mL of newly prepared AgNPs was added to each vial making the total volume 3mL. The contents of the vial were mixed properly and left as such for 2 minutes followed by recording of their visual and UV-vis spectral responses.The tap water showed positive response for Fe^{2+} in terms of naked eye as well as spectral both[Fig.4(a,b,c) main text].This was followed by the standard addition (60uL) of Fe^{2+} and Fe^{3+} respectively in all the above mentioned water samples followed by recording of visual as well as their spectral responses. All the three water samples showed visual as well as spectral responses.(Fig.4 main text)

2. Ferrous Ascorbate and Folic Acid Tablets were purchased from the market. One tablet was crushed and dissolved in 10mL of Millipore water(10000 ppm) solutions. From this stock solution corresponding 5000 ppm ,1000 ppm , 500 ppm , 100 ppm,10 ppm and 1 ppm solutions were prepared by dilution with Millipore water. All these solutions were checked for their probable interaction with AgNPs through visual and spectral responses. For this purpose 1 mL of AgNPs in separate vials were treated with 60 μL of Fe^{2+} solution of above mentioned concentrations (ppm) prepared from the iron tablet.As it is clear(Fig.4d, main text) that our AgNPs recognized the Fe^{2+} in the tablet at its 5000 and 1000 ppm level (visual as well as spectral responses). Nevertheless, the same AgNPs also gave spectral response for the 10000 ppm stock solution at comparatively higher wavelength with very high intensity as compared to 5000 and 1000 ppm solutions. Due to very high intensity the visual response was not clear(Fig.4d,main text).After that 10000 ppm solution of tablet was acidified with conc.HNO_3 followed by its drying over a hot plate. The same procedure was repeated twice. Finally 100 mL Millipore water was added and by this way the Fe^{3+} solution(1000 ppm) was prepared from the above mentioned tablet. This solution gave almost similar spectral response as we observed from the aqueous solution of Fe^{3+} in Millipore water.

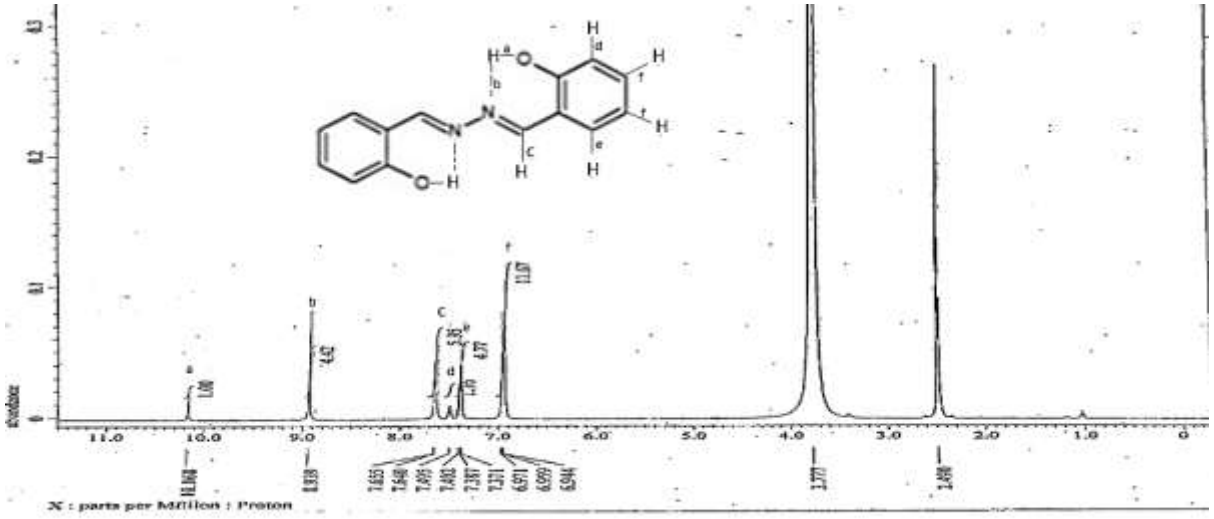
Figure S16: Photograph of the iron Tablet purchased from the market(For the recognition of Fe^{3+} /Fe^{2+} with AgNPs).

The Salicylazine was pepared by the literature procedure(Ref.no.43 main text)





(a)



(b)

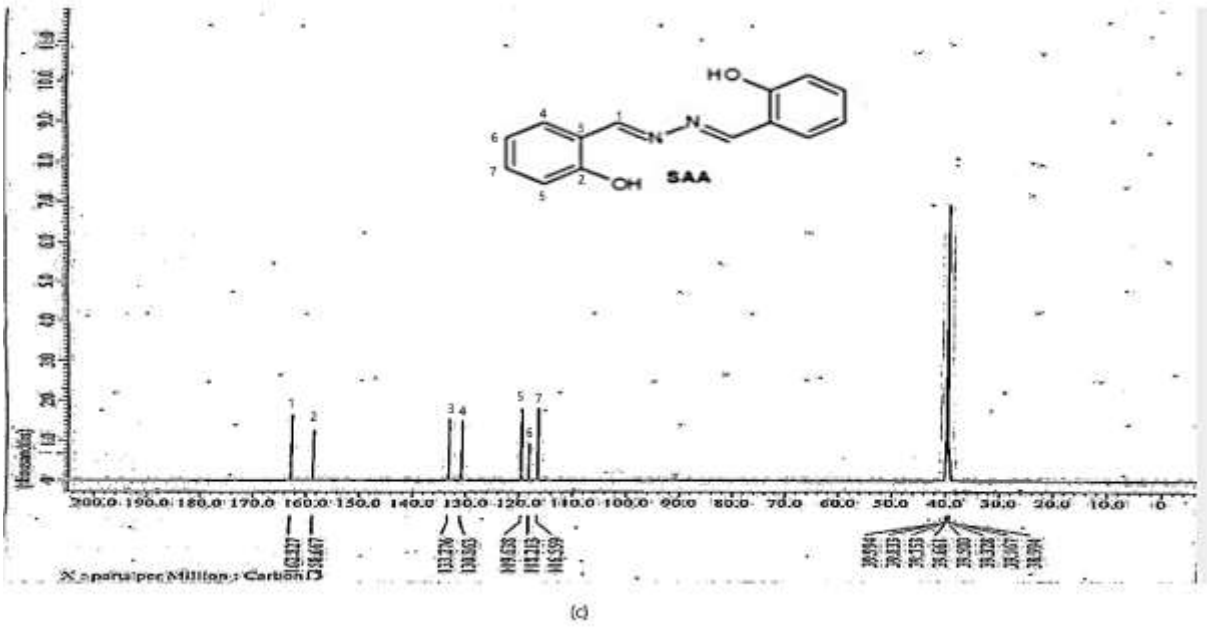


Figure S17: (a) IR , (b) ^{1}H NMR & (c) C^{13} NMR Spectra of Salicylazine.