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Research Article

COLORIMETRIC-BASED DETECTION OF NITRO AROMATIC EXPLOSIVES USING IRON 1, 10-PHENANTHROLINE

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ABSTRACT

Tris (1,10-phenanthroline) iron(II) hexafluorophosphate (Ferroin) was introduced to establish coincident detection of hazardous nitro aromatic explosives using the UV-vis spectroscopy method. Absorption properties of Ferroin have been investigated with different nitro compounds systematically, and the results indicated that Ferroin could behave as an effective sensor for picric acid (PA) high sensitivity and selectivity. The quenching mechanism has also been investigated in detail.

Keywords: UV-Visible, Sensor, 1 10, Phenanthroline, Nitroaromatic, Explosives.

1. INTRODUCTION

As powerful explosive compounds, TNP has raised global concerns about public safety and has severe deadly effects on human health and the surroundings. For the safety of the native nation and the protection of the environmental system, nitroaromatic explosives (NAEs) recognition is highly important [1, 2] Nitroaromatic explosives (NAEs) has been commonly used for military operations, preparation of landmines, and criminal activities. The hazardous effect of these NAEs can be seen by water and soil pollution which is very harmful for living organisms [3, 4]. Nitroaromatic compounds (NACs) are widely used as explosives [5, 6]. Picric acid (PA), is also an important element of nitroaromatic explosives (NACs) [7] and broadly used in rocket fuels, matches, glass, industries of leather, military explosives [8-10]. During the process they are released (directly or indirectly) into the environmental system which results in the pollution of soil, [11] water, and ecosystems [12] and results to lead a number of diseases such as skin irritation, nausea, hepatic and respiratory system disorder, etc. Hence, it is extremely required to generate technique for their detection that should be, sensitive, rapid and selective [13-15].

The 1,10 phenanthroline (Phen) possesses a high affinity for cation/anion due to antibonding orbitals which are low lying π* making them MLCT; that is metal-ligand charge transfer low energy electronic states [16, 17]. Many phenanthroline derived architectures have created mesmerizing molecular structures such as catenanes, rotaxanes, etc. Moreover, their planar structure stimulates intercalation with RNA and DNA, due to which they can be used for the recognition of DNA and RNA. Phen derivatives have also been explored for the preparation of pharmaceuticals, optoelectronic devices, analytical probes, and herbicides. Phen has the most active site towards nucleophilic reagents are reported to be the 2,9 and 4,7-positions; while, the positions of 5,6 or 3,8 are the site where electrophilic reagents preferentially here electron densities are found higher [18].

The parent phen can be detected as it gets absorbed in the wavelength of 200-300 nm of ultraviolet spectral region and with a low fluorescence quantum yield ($\Phi F=0.01$) displays a short emission of wavelength (λmax- 360 nm) [19, 20]. Furthermore, the photophysical properties of 1, 10 phenanthroline do not depend on the polarity of solvents which is an advantageous factor for its analytical properties. Several metal complexes of phen derivatives have been explored as chemosensors for cations/anions detection [21, 22]. We narrow our focus in this study to one specific organic complex of iron, named ferroin; when the iron center is in its second oxidation state (Fe^{2+}) and ferritin when in its third (Fe^{3+}). The main reason that this particular compound is so valuable because of the beautiful colour that it confers to aqueous solutions even at very low concentrations; aqueous ferroin solution has been observed with a deep red color whereas ferritin is noted to be blue This oxidative color change has been exploited in attempts to quickly query concentrations of compounds such as antioxidants, neurotransmitters, pharma-ceuticals, and biological metabolites in the aqueous phase, among other things [20, 23].

Ferroin solution is less toxic and non-corrosive, in addition to being a more useful indicator, with a color change from red to blue indicating a fickle film that should be renewed [24]. In non-aqueous liquids, ferritin and ferroin have been used successfully to query the reducing powers of edible oils, redox-coupled to their cobalt (II and I) analogs for use in a rechargeable redox-flow battery that has the potential to be optimized for efficient, large-scale energy storage [25].

Another particularly recent use of ferroin is as a DNA hybridization sensor, when covalently attached to a strand of DNA. In this report, a redox-coupled to ferrocene, which is covalently attached to another strand of differing sequence has been reported [26-28]. However, there is no such report of Iron-based 1,10 phenanthroline (F1) towards the sensing of picric acid. Herein, we have reported Iron-coordinated 1,10 phenanthroline (Ferroin-F1) as a highly sensitive and selective sensing probe towards PA (picric acid). The sensing nature of F1 towards PA is investigated by UV-vis spectroscopy and the sensitivity is measured by LOD.

2. EXPERIMENTAL

2.1. Material and Instrumentation

Chemicals and solvents used in the experiments are commercially available. Ferroin was directly purchased from Sigma-Aldrich and along with other chemicals used without any further purification. The common reagents and solvents were obtained from Merck and S. D. Fine Chem. Ltd. Solvents were distilled following the standard literature methods before their use. Spectrophotometric measurements were performed by a quartz cuvette using a path length of 1 cm on a Varian UV-vis spectrophotometer (model: Cary 100 Bio).

2.2. Detection experiments of PA

Colorimetric detection of PA was performed according to the following procedure: First, 0.10 µM nitro compound solutions were added into a 2 ml solution of 1 (0.5 mM). In a typical procedure, a dispersed aqueous solution of F1 (Iron 1,10phenanthroline; 0.5 mM) was prepared. Further, a 3 mL aliquot of this aqueous solution was employed in a 1 cm width quartz cuvette, and the absorbance response was recorded in the range of 200-800 nm. The Absorbance experiments were conducted after the periodical addition of freshly prepared nitro aromatics.

For the quenching titration experiment 20-100µM prepared solution was taken. The luminescence spectra of F1 in the presence of PA were recorded in water. Upon adding different quantities of PA, resultant that the characteristic emission of the F1 (singlet state) at λ-510 nm is heavily quenched with a considerable color change suggesting the formation of a non-emissive complex.

3. RESULTS AND DISCUSSION

3.1. Photo physicalBehavior of Ferroin (1)

The aqueous solution of the ferroin complex results as red colored and has a band of broad absorption in the visible region with maximum absorption at 510 nm and the molar absorptivity is 11,100 l mol^{-1} cm^{-1} with Eg=4.038 eV band gap value. (fig.1)

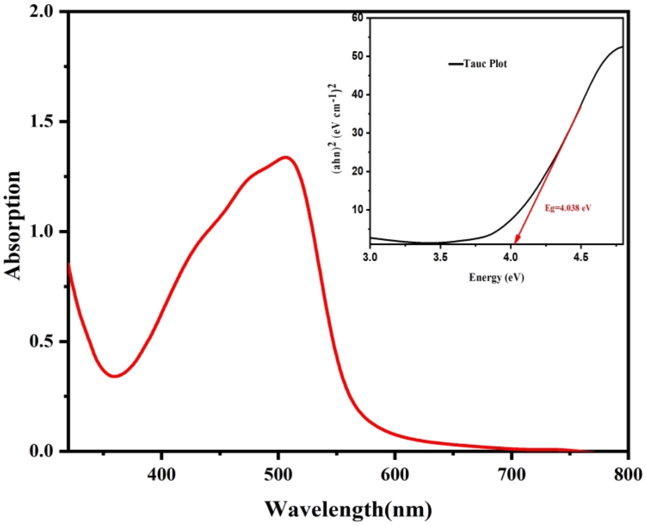
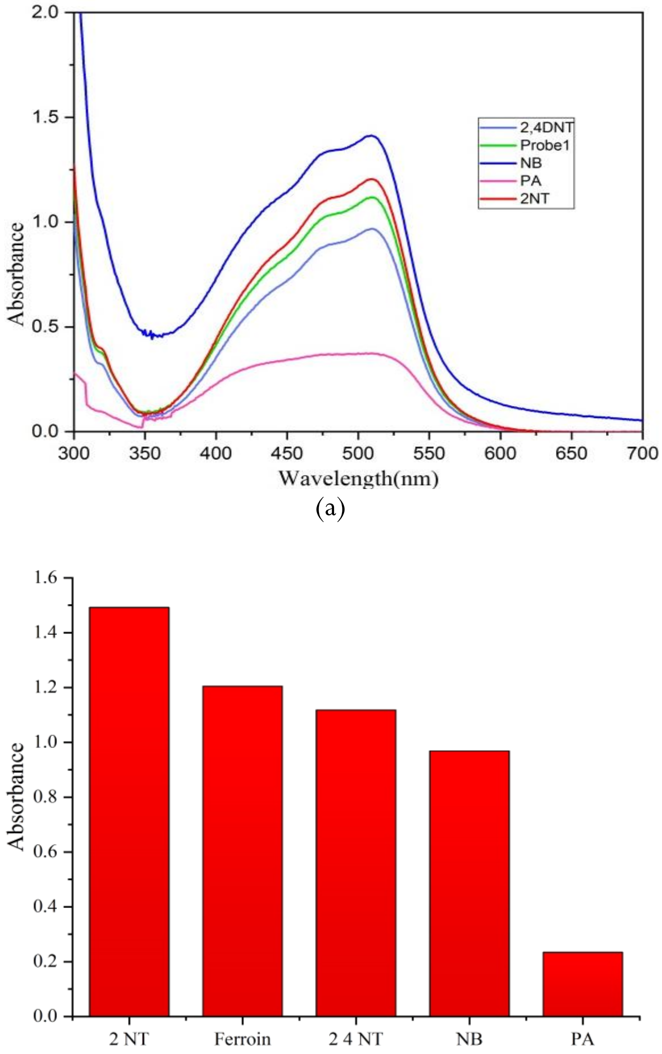


Fig. 1: Absorption spectrum of ferroin (F1) with the bandgap value (inset Tauc Plot)

3.2. Interaction of F1 with PA

The absorption spectrum of F1 in H_2O displays the maximum absorbance at 510 nm wavelength. To examine the selectivity of 1, the absorption spectra were recorded by the analytes additions such as 3-NT (Nitrotoluene), 4-NT, Dinitrotoluene (2,4-DNT), 2,4,6-Trinitrophenol (PA), and NB (Nitrobenzene) into the aqueous solution of F1 separately. Interestingly, a significant hypochromic shift was detected in the case of Picric acid (fig. 2(a)) and color change was observed from pink to violet which proves the colorimetric sensing behavior of F1 towards picric acid. The addition of other compounds did not show any significant change in the UV-Vis spectra of F1 (fig. 2(b)). Most nucleophilic position present in phen ring attracts electron deficiency moiety. This observation proves that F1 effortlessly senses more electronic-deficient analysts and found to be that F1 would be a selective sensor of nitro aromatics 7, 14, 29]. PA is the most electronic deficient compound which showed a significant affinity towards F1.



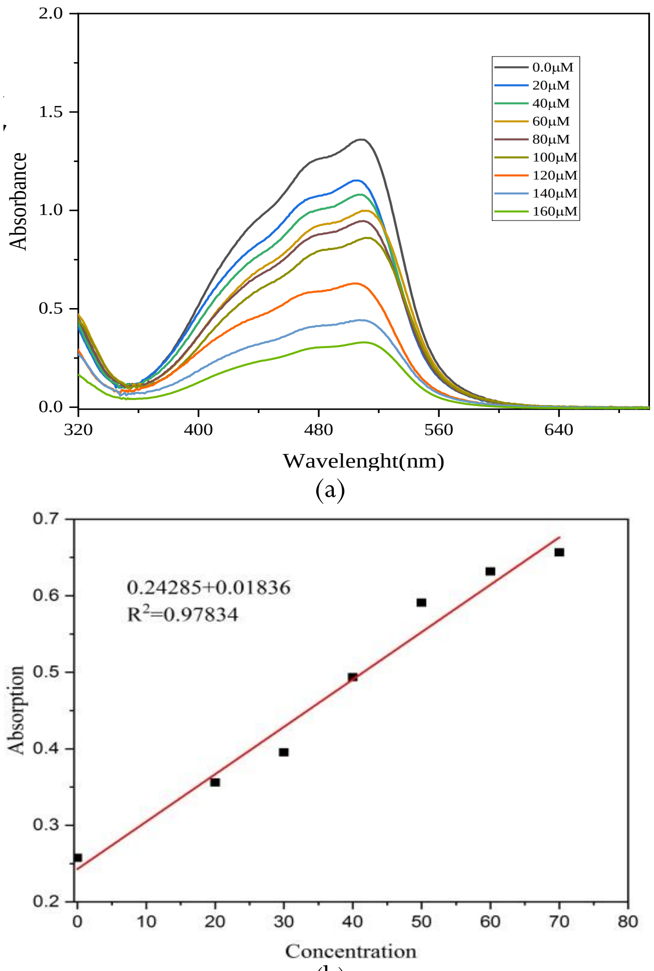
(a)

(b)

Fig. 2: (a) UV-visible absorption spectra of F1 in the absence and presence of NACs in water (b) Plot of normalized absorbance of 1 (at 510 nm) upon addition of various NACs

Furthermore, we performed absorption titration of F1 against PA with different concentrations. The coordination complex formation method has been assumed for the detection of Picric acid present in aqueous medium, and color change of resultant also has been noticed. For complex formation, different concentrations (0-160 μM) of picric acid solutions were used. The subsequent addition of PA into the solution of 1 results in a gradual decrease of the absorption peak at 510 nm. (fig. 3(a)). This phenomenon suggested that with the increase in the concentration of PA, complex formation also enhanced with F1 and it might be by the H bonding.

The concentration of PA was found to be linear with the change in UV-Visible absorbance relations (Ex-645/510). The resultant calibration curve in ratio of these two peaks (Ex-645/510) the absorption coefficients versus concentration of picric acid enables one to estimate the quantitative presence of PA present in water in μM levels (fig. 3b).



(a)

(b)

Fig. 3: (a) UV-Vis spectrum of probe F1 at changing concentrations of PA (b) Calibration curves between absorption vs. concentration of PA

The colored complex with a peak of 510 nm is detectable by the human eye. The sensitivity was characterized by the limit of detection. The limit of detection (LOD) is calculated using the equation $\mathrm{LOD} = 3.3(\sigma/S)$, where σ is the standard error and S is the slope of calibration. The limit of detection (LOD) of 1 with PA was found to be 0.27nM

4. CONCLUSION

In conclusion, we have successfully examined an extremely stable ferroin indicator for quick and sensitive detection of nitro aromatic explosives through the UV-Vis absorption spectroscopy technique. Remarkably, it can easily detect PA through the naked eye. This absorption intensity is recognized to photo induced electron transfer and resonance energy transfer. This work shows a promising approach to colorimetry based sensors for explosives; this will possibly be beneficial under further truthful conditions in the future.

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Conflict of interest

None declared

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