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Design and Synthesis of Fluorochemosensors and their Cation Recognition Study

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***Abstract*: The fluorescence of organic molecules depends sensitively on their atmosphere. Fluorescent dyes have for that reason developed into popular molecular probes for the selective recognition of metal ions. In this study, rhodamine B hydrazide was used as a fluorescent chemodosimeter for Cu^{2+} ion. This rhodamine B hydrazide can identify Cu^{2+} selectively, and Cu^{2+} promoted hydrolysis can afford fluorescent rhodamine B molecule as a product. They verified that this system can sense 10 nM Cu^{2+} within 2 min (pH = 7). Previous work resulted in a great interest being given to the application of the ring-opening and closing processes of rhodamine B derivatives to fluorescent chemosensors. Limitless research groups have worked on the rhodamine-based fluorescent chemodosimeter and it is not possible to contain all the examples of this type in this part. However, we are given that some examples of Rhodamine-based fluorescent sensors for detection of Cu^{2+}, Hg^{+}, Zn^{2+}, Pb^{2+}, Cr^{3+}, Fe^{3+} and Pd^{2+} in solutions. Cinnamaldehyde - rhodamine based signalling systems were designed and synthesized for the selective recognition of Fe^{+3} ions. The cinnamaldehyde molecule was used as a recognition moiety and rhodamine-B was used as a signalling moiety. The excellent fluorescent response to Fe^{+3} in ACN solution can be detected even by the naked eye, which provides a facile method for the visual detection of Fe^{+3}. Complexation of the Fe^{+3} ions opens the spirolactum ring of rhodamine moieties to produce specific colour change as well as fluorescence development.**

***Keywords*: Fluorescence and phosphorescence, Design of fluorescent molecular sensor, Fluorescent chemosensors based on rhodamine, Synthesis of chemosensors SAR-31 and SAR-27.**

1. Introduction

Fluorescence spectroscopy and ultraviolet techniques have been applied to various analytical, bio-analytical, environmental, medical and forensic investigations. Several analytical methods that are offered for recognition of target concerned such that flame photometry, AAS, HPLC, mass spectrometry, ion sensitive electrode, microprobe analysis, neutron activation analysis, have been developed [1-4]. But these methods are expensive and time uncontrollable process that involves complicated instrumentation and do not allow permanent monitoring [11]. If the target compound exhibit phenomenon called as Luminescence where the emission of electromagnetic radiation of longer wavelength to that of absorbed radiation can be seen are analysed by using the modern spectroscopic technique called as 'flourimetry' [5]. Hence, significant hard works are life form complete to develop selective fluorescent sensor for recognition of targeted species [10]. A large number of substance are recognized which absorb take up ultraviolet or visible light energy. But these substances are unable to find overload energy as heat through collisions with near atom or molecules. But a number of significant substances are too known which lose only fraction of this overload energy absorbed. This method of emitting radiation is cooperatively known as luminescence [8]. Luminescence is an emission of UV/visible or infrared photons from an electronically excited species [9]. Luminescence light created at low temperatures. Therefore, the light shaped by this procedure is regarded as "light without heat" or "cold light". Luminescence is cold light but incandescence is hot light [6]. Emission of radiation while there is transition of electron from singlet excited state to singlet ground state is known as fluorescence. The wavelength of absorbed radiation is called as excitation wavelength and that of emitted radiation is called as emission wavelength [7].

The first and simplest coronand PET sensor 1 was reported by de Silva *et al* [12]. Upon binding with K^{+} in methanol fluorescence quantum yield of PET sensor 1 increase from 0.003 to 0.14 in to the sensor 2 [13]. The methoxy groups are ortho position to the nitrogen atom of the crown join in the complexation to complete strong binding with Na^{+} and accompany with switching 'on' the fluorescence. This was a balanced result from the proton signaling structure 3 [14-15]. The uncomplicated amine group within 2 was elaborate into azacrown ether in 1 for the purpose of signaling alkali cation. The podand-based sensor 4 [16] have polyamine chain and used for the binding of Zn^{+2}, on the other hand it also shows strong binding with Cu^{+2}. Two PET dynamic receptors were also present within 5 [17]. The anthryl-9, 10-dimethyl turn has also feature in Fabbrizzi's propose for the fluorescent sensing of imidazole derivatives [18] though the anthryl-8, -dimethyl back has been oppressed by Vance and Czarnik for sensing pyrophosphate [19]. The transition metals exhibit redox activity

and electron transfer can occur from the fluorophore to the bound metal ion, or vice versa, which results in quenching of the fluorophore by non-radiative energy transfer according to the Dexter mechanism in which a metal ion can quench the fluorescence of the excited state of the fluorophore by an energy transfer mechanism [20, 21].

Rhodamine was first synthesize by Noelting and Dziewonsky in 1905 [24] and have been widely use as fluorescent probe for the detection of different ions, in the lasing medium in dye lasers and fluorescent marker in biological studies [22, 23, 25]. In 1997 Czarnik and co-workers reported a pioneer occupation on the rhodamine B derivative moreover its ring cavity mechanism for the selective detection of Cu^{2+} ion [26].

In this study, rhodamine B hydrazide was used as a fluorescent chemodosimeter for Cu^{2+} ion. As illustrated in the Figure 1.7 this rhodamine B hydrazide can identify Cu^{2+} selectively, and Cu^{2+} promoted hydrolysis can afford fluorescent rhodamine B molecule as a product. They verified that this system can sense 10 nM Cu^{2+} within 2 min (pH = 7). Czarnik's work resulted in a great interest being given to the application of the ring-opening and closing processes of rhodamine B derivatives to fluorescent chemosensors. Limitless research groups have worked on the rhodamine-based fluorescent chemodosimeter and it is not possible to contain all the examples of this type in this part. However, we are given that some examples of Rhodamine-based fluorescent sensors for detection of Cu^{2+}, Hg^{+}, Zn^{2+}, Pb^{2+}, Cr^{3+}, Fe^{3+} and Pd^{2+} in solutions.

A rhodamine 6G derivative **6** was synthesize and used to classify Cu^{2+} in an aqueous standard [27]. Below optimized environment, the quantification of Cu^{2+} as a result of **6** using an absorption method was reasonable in the linear effective range 0.05- 5.00 μM, with a 1finding limit of 10 nM for Cu^{2+} and superb recognition of the other metal ions. Kim and co-workers reported the design and synthesis of an innovative rhodamine-based molecular sensor **7**, manners and N-butyl-1,8naphthalimide group [28]. **7** show selective colorimetric and fluorescence "turn-on" change at 550 nm by a rhodamine ring-opening advance in the direction of Cu^{2+} ion. It is report that **7** forms 2:2 complex with Cu^{2+} ion. Zeng *et al* [47] report 4-[{(E)-N-(-(rhodamine 6G lactam)-ethylenediamineimino} methyl] benzene-1,3-diol (8), which show a reversible, selective, and sensitive fluorescence development response to Cu^{2+} in HEPES buffer (20 mM, pH 7.0) contain 50% (v/v) CH_3CN. Mashraqui et al. [29] comprise synthesized a rhodamine 6G based chromo and fluorogenic survey 9, which be capable of identify micromolar concentrations of Zn^{2+} with revolving the colour of the solution from colourless to orange and moreover as a result of change the matching absorption maximum from 302 to 528 nm.

Yang *et al*. include designed a novel bifunctional colorimetric and fluorescent chemosensor. It shows considerable "off–on" fluorescence accompanies by resources of color changes from colorless to red ahead binding with Hg^{2+} ions and strong emission of 583nm [31]. The spectral answer of compound 10 toward Hg^{2+} was demonstrated to be reversible and robust against interference from other metal ions. Das *et al*. report a rhodamine 6G base on chemosensors 11 for the recognition of $Hg^{2+}$and Cu^{2+}. Here H_2O-MeOH (1:1, v/v) solution at pH 7.0, both Hg^{2+} and Cu^{2+} induce colour changes amid new absorption peaks to appear at 534 nm for Hg^{2+} and 528 nm for Cu^{2+} [30].

Liu *et al*. have reported a new rhodamine B-based fluorescent chemosensor 13 study. for Hg^{2+} [32]. Song et.al utilize an irremediable desulfurization reaction to assemble up a new fluorescent ratiometric chemosensor 14 based on the FRET, which would be used to the detection of Hg^{2+} in aqueous medium [33]. Shiraishi *et al*. in recent times report a rhodamine diacetic acid derivative 15, which show burly green fluorescence in CH_3CN with Cu^{2+} while screening very feeble orange fluorescence with other metal ions. [34] Tae and Bae utilize the information that siderophores include hydroxamates as binding sites for Fe^{3+} [35]. Huang and co-workers demonstrated a rhodamine hydrazone derivative 17, which is a turn-on fluorescent sensor for Fe^{3+} metal ions. Moreover, the derivative 17 was used to sense Fe^{3+} within living cells [36]. Lin *et al*. describe rhodamine derivative 18 as a fluorescent sensor for the recognition of gold ion in Au^{3+}-mediated hydrolysis of acylsemicarbazide to carboxylic acid [37].

Choosy recognition of biologically imperative metal ions has greatly gained its importance because metal ions are occupied in a multiplicity of fundamental biological process in organisms. Iron is one of the mainly important metals in the biological system and acting a key role in various biochemical processes at the cellular level. Specially, ferric ion (Fe^{3+}) is extensively retained in many proteins and enzymes also for structural purposes or as piece of a catalytic site [40]. Additionally, the ferric ion is eminent as a fluorescence quencher due to its paramagnetic nature, and mainly of the reported Fe^{3+} receptors, such as analogues of ferrichromes or siderophores, feel a fluorescence quenching when leap with Fe^{3+} [41], while it is usually supposed that probes with a fluorescence development signal when interacting with analytes are greatly further efficient. Consequently, the improvement of new fluorescent indicators for perfect and specific detection of Fe^{3+}, particularly those that exhibit selective Fe^{3+} -improved emission, is still a challenge. Freshly, a few sensors have been described to exhibit a turn-on response to Fe^{3+} ions [42, 43].

Cinnamaldehyde is creating in numerous active compounds. Payable to its simple research and its biological activity, cinnamaldehyde and metal complexes have expected extensive attention in coordination and medicinal chemistry. Cinnamaldehyde can from a variety of Schiff and report to be superior reagent in various biological and numerous applications. A literature survey shows that only a few attemps have been made for the synthesis of fluorescent sensors contain

cinnamaldehyde as a recognition moiety for metal ions. In this chapter, we include synthesized rhodamine 6G and rhodamine B based fluorescence molecular sensor use cinnamaldehyde as the detection moieties.

2. Experimental Work

A. Materials and physical measurements

All chemicals and solvents involved were of analytical grade. All metal nitrate salts and chloride salts were provided by college from Finar Chemical (India) Pvt, Ltd. and ACS Chemicals Rhodamine 6G was purchased from Spectrochem and ethylenediamine from ACS Chemicals. Cinnamaldehyde were obtained from Spectrochem Pvt. Ltd. Mumbai. Hydrazine hydrate and Rhodamine B were purchased from Finar and Sisco Research Lab respectively. Acetonitrile was purchased from Merck Life Science Pvt. Ltd.

^{1}H and ^{13}C NMR spectra were recorded with Avance-III 400 MHz Bruker FT-NMR Instrument. FT-IR spectra were recorded as the KBr pellet on the Perkin Elmer Fourier transform (FT-IR) spectrum RX 1 spectrometer. Mass spectra were recorded on a Q-TOF Micro™ LC-MS instrument. The UV/Vis spectra were recorded on a UV-1700 pharmaspecScan (Shimadzu).

B. Synthesis of chemosensors SAR-31 and SAR-27

1) Synthesis of SAR-31

Ligand SAR-31 Rhodamine B (2.0g, 4.1mmol) dissolved in 22.0ml methanol follow by edition of hydrazine hydrate (1.46g, 29.16mmol). The reaction mixture was stirred and heated to reflux for 6 hours. Till the fluorescence solution disappears. The reaction was cooled to room temperature and the solid mass was washed with 10.0ml cold methanol (Intermidate-1). This reaction maintained of 1:15 ratio.

Intermidate-1 (0.5g, 1.09mmol) and cinnamaldehyde (0.144g, 1.08mmol) dissolved in 5.0ml methanol. The reaction mixture was stirred and heated to reflux for 6 hours. The reaction was cooled to room temperature and the solid masses washed with 10.0ml cold methanol and afford SAR-31 as a white solid. This reaction maintained of 1:1 ratio. ^{1}H NMR ($CDCl_3$, 400 MHz), δ 1.120-1.185 (t, 12H), δ 1.741, δ 3.268-3.370 (q, 8H), δ 6.239-6.282 (d, 2H), δ 6.433 (s, 1H), δ 6.519-6.562 (d, 2H), δ 6.623 (s, 1H), δ

6.809-6.890 (t, 1H), δ 6.933 (s, 1H), δ 7.029-7.072 (d, 2H), δ 7.231-7.322 (t, 5H), δ 7.414-7.432 (d, 2H), δ 7.967-8.004 (d, 1H), δ 8.161-8.206 (d, 1H) ppm; LC-MS (m/z): pick $[M]^+$ at 570.47, $[M+1]^+$ peak at 571.47, $[M+2]^+$ peak at 572.43, $[M+Na]^+$ peak at 593.45, $[M+K]^+$ peak at 609.43.

2) Synthesis of SAR-27

Ligand SAR-27 Rhodamine 6G (1.0g, 2.08mmol) dissolved in 22.0 ml ethanol follows by edition of hydrazine hydrate (1.044g, 20.85mmol). The reaction mixture was stirred and heated to reflux for 6 hours. Till the fluorescence solution disappears. The reaction was cooled to room temperature and the solid mass was washed with 10.0ml cold ethanol (Intermidate-2). This reaction maintained of 1:10 ratio.

Intermidate-2 (0.15g, 0.34mmol) and cinnamaldehyde (0.04g, 0.30mmol) dissolved in 5.0ml ethanol. The reaction mixture was stirred and heated to reflux for 6 hours. The reaction was cooled to room temperature and the solid masses washed with 10.0ml cold ethanol and afford SAR-27 as a white solid. This reaction maintained of 1:1 ratio. ^{1}H NMR ($CDCl_3$, 400 MHz), δ 1.241-1.350(t, 6H), δ 1.879 (s, 6H), δ 3.164-3.268 (q, 4H), δ 3.505(s,2H), δ 6.360 (s,2H), δ 6.409 (s,2H), δ 6.481 (s,1H), δ 6.562 (s,1H), δ 6.786-6.864 (t,1H), δ 6.915 (s,1H), δ 7.013 (d,1H), δ 7.231-7.303 (t,5H), δ 7.142 (d,2H), δ 7.97-8.01 (d,2H) ppm. LC-MS (m/z): $[M]^+$ at 542.40, $[M+1]^+$ at 543.40, peak at, $[M+2]^+$ peak at 544.40 , $[M+3\ ]^+$ peak at543.40, $[M+K]^+$ peak at 681.86.

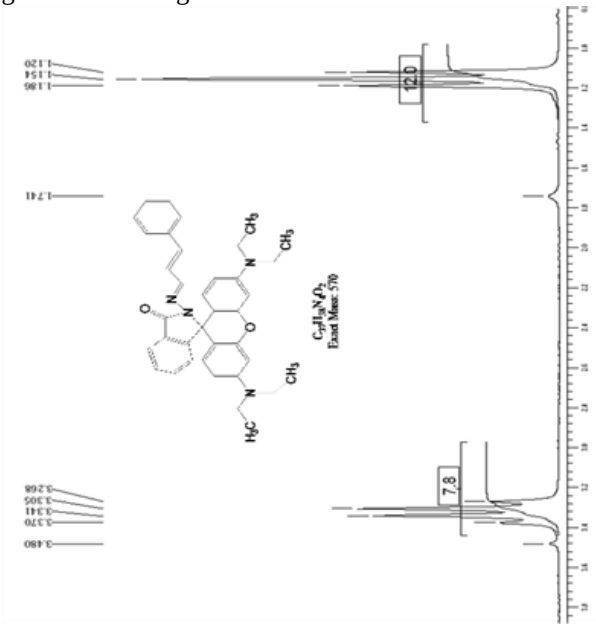
3) Ion bonding study

Stock solution of compound SAR-31 (2×10^{-4}M) were prepared by dissolving the compounds in acetonitrile. Solutions of nitrate and chloride salts (2×10^{-4}M) of various cations (Na^+ , k^+ , Ni^+ ,Pb^{2+} , Co^{+2} , Cu^{+2} ,Fe^{+3} , Cr^{+3} ,Zr^{3+}, and Al^{+3}) were prepared in acetonitrile solution . Then 5.0ml of stock solution of SAR-31 and 5.0ml of stock solution of metal salt added to a 10.0ml volumetric flask. Compound SAR-31 is binding only with Fe^{3+} metal ion, Cr^{3+} and Cu^{2+} only gives colour solution they are not binding with Compound SAR-31.

3. Results and Discussion

A. Syntheses and Characterizations

The synthetic route for the compound SAR-31 and SAR-27 is shown in scheme 1.1 and scheme 1.2. This were synthesized and characterized on the basis of analytical and spectroscopic data. The ^{1}H NMR spectra of SAR-31 and SAR-27 are shown in Figure 1.13 and Figure 1.14.



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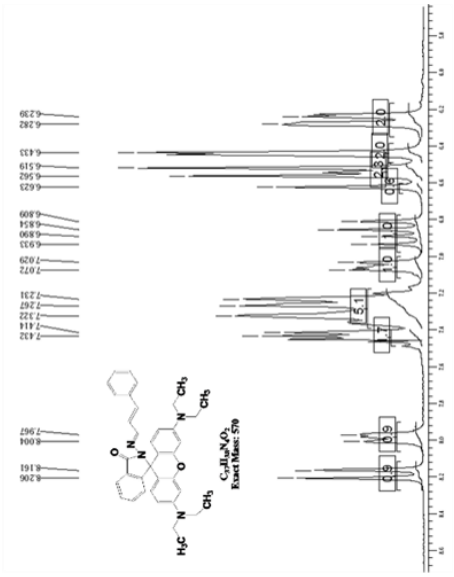


Fig. 1. ^{1}H NMR spectra of SAR-31

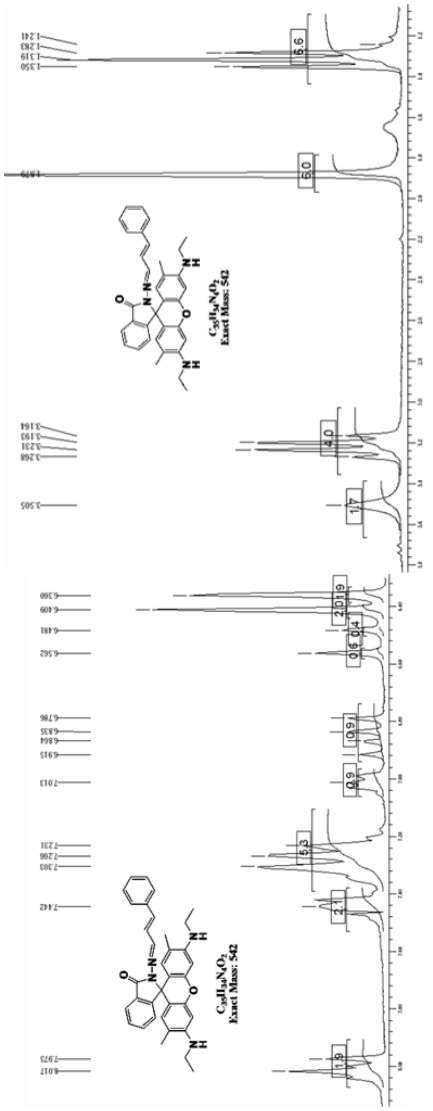


Fig. 2. ^{1}H NMR spectrum of SAR-27

Table 1
^{1}H NMR of SAR-31

Δ	Multiplicity	Number of hydrogen
1.120-1.185	Triplet	12H
3.268-3.370	Quartet	8H
6.239-6.282	Doublet	2H
6.433	Singlet	1H
6.519-6.562	Doublet	2H
6.623	Singlet	1H
6.809-6.890	Triplet	1H
6.933	Singlet	1H
7.029-7.072	Doublet	2H
7.231-7.322	Doublet	2H
7.414-7.432	Doublet	2H
7.967-8.009	Doublet	1H
8.161-8.206	Doublet	1H

Table 2
^{1}H NMR of SAR-27

Δ	Multiplicity	Number of hydrogen
1.241-1.350	Triplet	6H
1.079	Singlet	6H
3.164-3.268	Quartet	4H
3.505	Singlet	2H
6.360	Singlet	2H
6.409	Singlet	2H
6.481	Singlet	1H
6.562	Singlet	1H
6.786-6.915	Triplet	1H
7.231-7.303	Triplet	5H
7.442	Doublet	2H
7.973-78.017	Doublet	2H

The mass spectrum of SAR-31 shows molecular ion peak $[M]^+$ at 570.47, $[M+1]^+$ peak at 571.47, $[M+2]^+$ peak at 572.43, $[M+Na]^+$ peak at 593.45, $[M+K]^+$ peak at 609.43, which agreed well with the proposed structure. Mass spectra of SAR-31 presented in the figure 3.

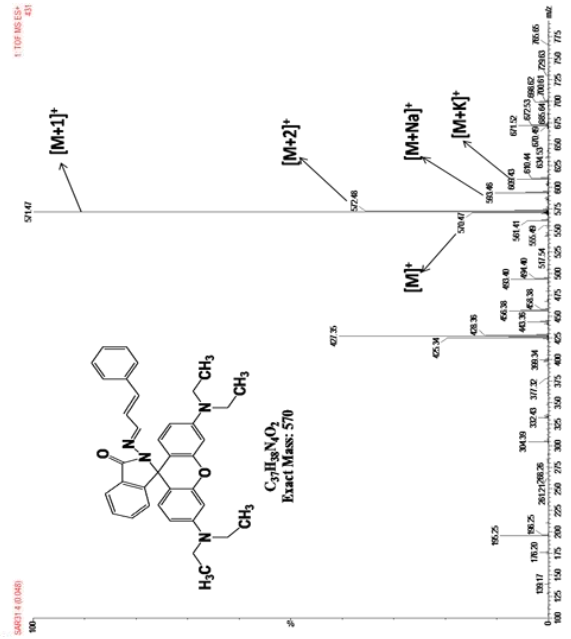


Fig. 3. LC-MS of SAR-31

The mass spectrum of SAR-27 shows molecular ion peak $[M]^+$ at 542.40, $[M+1]^+$ at 543.40, peak at, $[M+2]^+$ peak at 544.40 , $[M+3]^+$ peak at543.40, $[M+K]^+$ peak at 681.86 , which agreed well with the proposed structure. Mass spectra of SAR-27 presented in the figure 4.

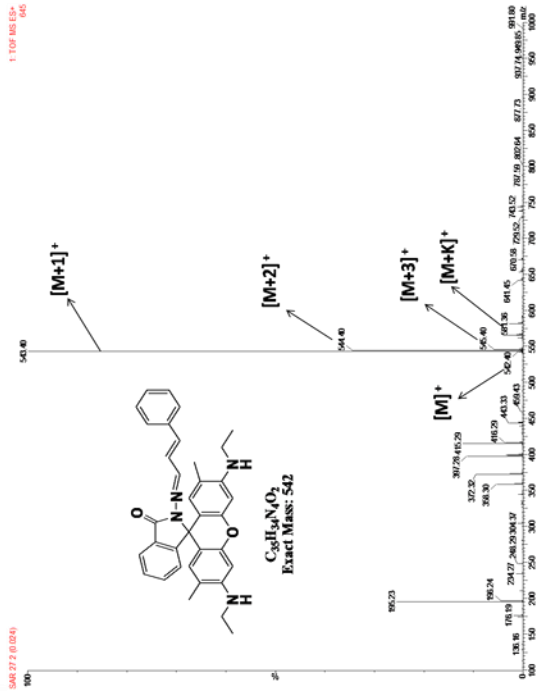


Fig. 4. LC-MS of SAR-27

The synthetic route for the compound SAR-31 and SAR-27 is shown in scheme 1.1 and scheme 1.2. This were synthesized and characterized on the basis of analytical and spectroscopic data. The IR spectra of SAR-31 and SAR-27 are shown in figure 5 and figure 6.

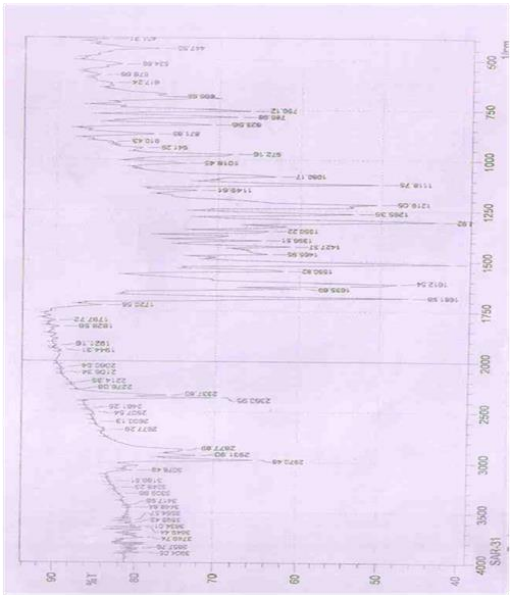


Fig. 5. IR Spectrum of SAR-31

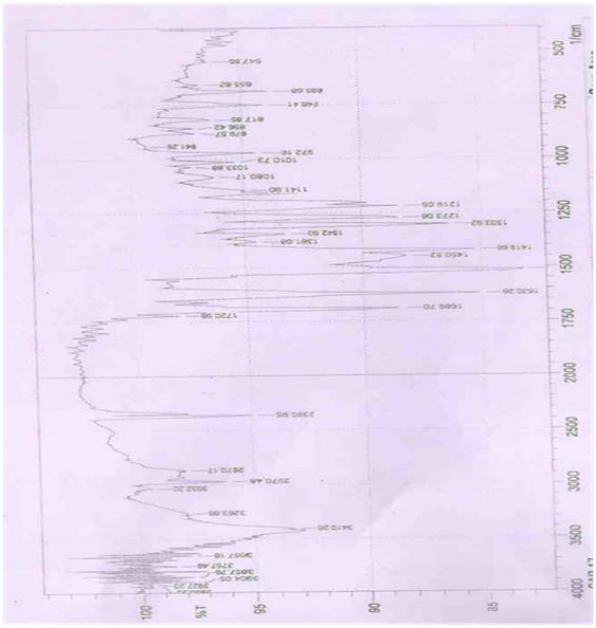


Fig. 6. IR Spectrum of SAR-27

Table 3
IR of SAR-31

Frequency(cm^{-1})	Interpretations
1720	C=O carboxylic acid
1681	C=C Alkene
1635	N-H (bend)
1612	N-H (bend)
1465	$-CH_2-$ (bend)
1350	C-N Amines
1303	C-O carboxylic acid
972,941,879,856,817	$-CH_3-$ (out-of-plane bend)
748,686,655	C-H Aromatic (out-of-plane bend)

Table 4
IR of SAR-27

Frequency(cm^{-1})	Interpretations
3410	N-H (stretch)
3263	N-H (stretch)
3032	C-H (Stretch)
2970	C-H (Stretch)
2870	C-H (Stretch)
1689	C=O Amide
1620	C=C
1450	$-CH_3$ (bend)
1342	C-N Amines
1303	C-N Amines

The fluorescence and UV-Vis spectra of the fluoroionophores SAR-31 was recorded in acetonitrile solution at room temperature. Compound SAR-31 in acetonitrile solution be nonfluorescent, representing that spirolactam form exist predominantly. Earlier reports reveal that certain transition-metal ions bind selectively with appropriate derivatives of rhodamine, where metal-ion binding induces opening of the spirolactam ring and generation of the xanthene form, with associated changes in the electronic and fluorescence spectral patterns. Thus, we checked the binding affinity of SAR-31 near all common metal ions, e.g. $^+$, k^+, Ni^+,

Pb^{2+}, Zr^{2+}, Co^{+2}, Cu^{+2}, Fe^{+3}, Cr^{+3}, and Al^{+3}, Zr^{2+}, (10 equivalent) by observe changes in the electronic and fluorescence spectral pattern in an acetonitrile medium. The spectral modify for SAR-31upon addition of various metal ions is shown in figure 7. Behind the adding of metal ions, UV/vis absorption spectra show a distinct change and the appearance of an innovative spectral band with a maximum at 530 nm for Fe^{3+} ions. The absorption band at 530 nm in the case of Fe^{3+} is unpaid to the formation of delocalized xanthane moiety of rhodamine by selective Fe^{3} induce ring opening of spirolactam, which also clarify the change in color from pink to Orange in the presence of this Fe^{3+} ion. Without metal ions SAR-31 show almost no fluorescence upon excitation at 530 nm, suggesting that SAR-31 exist in a ring closed nonfluorescent spirolactam conformation. The addition of Fe^{3+} creates fluorescence upon excitation at 530 nm, indicating complexation of Fe^{3+} with SAR-31. In other words, free SAR-31 was non-emissive, but their fluorescence can turn from "off" to "on" when Fe^{3+} ions were added.

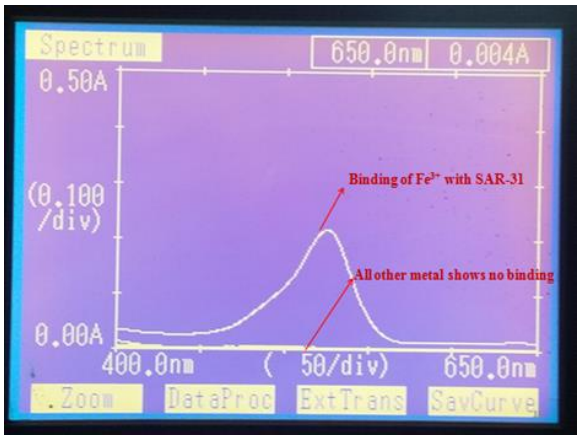


Fig. 7. Compound SAR-31 to binding different metal ions (10 equivalents) in acetonitrile solution

B. *Stoichiometry and binding mode study*

2×10^{-5}M solution of SAR-31 and metal Fe^{3+} were prepared in acetonitrile solution. Then 10ml volumetric flask were labeled in which 1ml,2ml….10ml metal ion of Fe^{3+} solutions were filled and volumetric were made 10 ml using SAR-31 solution. The mixture was shaken properly and was kept stable for about 2 hours, after which its absorbance in U.V spectrometer was measured.

The Job plot with deference to 400nm-600nm showed that the absorbance attain a highest at a molar fraction of ~ 1/1, indicating to a 1:2 stoichiometry was most possible for the binding of Fe^{3+} with SAR-31 (*see* Figure 8.). It is found in the literature that the majority of rhodamine based fluorescent chemosensors show a 1:1 binding stoichiometry of Fe^{3+} and fluorescent chemosensors [44, 45, 46]; here are only a few reports of the 1:2 binding of Fe^{3+} and fluorescent chemosensors [46, 47]. In the fluorescent chemosensors described here, binding stoichiometry is 1:2 for Fe^{3+} and SAR-31.

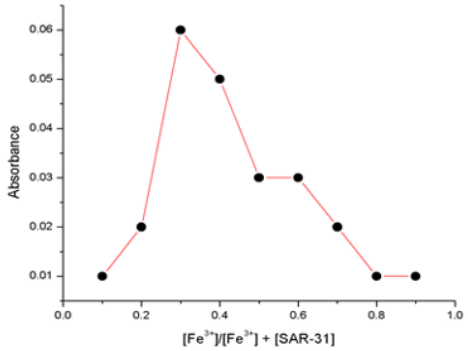
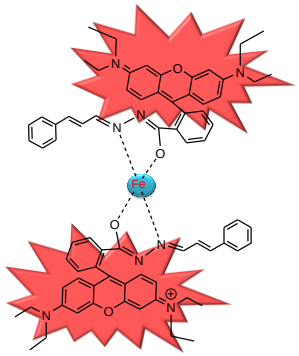


Fig. 8. Job plots of SAR-31 with Fe3+ in acetonitrile solution from the jobs plot we can conclude that 1:2 binding is observed

The two rhodamine-Cinnamaldehyde ligands attach one metal ion of Fe^{3+} as shown in scheme 1.3.



Scheme 1.3. proposed binding structure of SAR-31 with Fe^{3+}

Consider the behaviours of the fluorescence and absorption spectra, the off–on reply of SAR-31 possibly will be explained by the spirocycle open–close mechanism. The free check out SAR-31 is in the spirocyclic outline, which is nonfluorescent, while coordination of Fe^{3+} leads to spirocycle opening, resulting in the look of visible absorption and fluorescence. The visible change in color is able to be used for the "naked-eye" recognition of Fe^{3+} ions in an acetonitrile solution environment (*see* Figure 9.). Compounds SAR-31 proves similar type of selectivity towards metal ions.

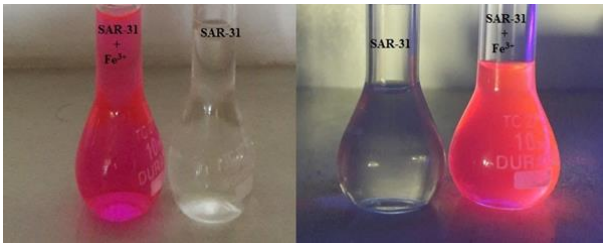


Fig. 9. Change in colour (Left) and fluorescence (right) of SAR-31 in acetonitrile solution with Fe^{3+} ions and blank

4. Conclusion

In outline, cinnamaldehyde-rhodamine based signalling systems were designed and synthesized for the selective

recognition of Fe^{+3} ions. The cinnamaldehyde molecule was used as a recognition moiety and rhodamine-B was used as a signalling moiety. The excellent fluorescent response to Fe^{+3} in ACN solution can be detected even by the naked eye, which provides a facile method for the visual detection of Fe^{+3}. Complexation of the Fe^{+3} ions opens the spirolactum ring of rhodamine moieties to produce specific color change as well as fluorescence development.

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