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FLUORESCENT SCHIFF BASE CHELATORS: A CRITICAL REVIEW ON THEIR SENSING ABILITIES FOR METAL IONS AND CYANIDE ION

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ABSTRACT

This review article provides a thorough investigation into the use of Schiff base derivative probes for the identification and elimination of metal ions, specifically aluminium, mercury, copper, zinc, iron (III), and magnesium, in conjunction with cyanide. When these probes chelate with these metal ions, they exhibit unique fluorescence activity, functioning as on-off switches. In order to highlight how crucial it is to identify these ions in biological and environmental settings, the review carefully looks at the characteristics and detection limits related to each metal ion-chelate complex. The article also explores how well these probes work to remove metal ions. This review attempts to provide light on the potential of Schiff base derivatives for accurate detection, effective removal, and the critical factors influencing these processes by closely examining their fluorescence activity and characteristics.

Keywords: fluorescent schiff base chelators, metal ions, fluorescence activity

INTRODUCTION

Human exposure to metal ions has become a necessary part of daily life in the modern period,

with grave effects for both the environment and human health. When aluminium is present in the

biological system as Al^{3+} , it exhibits strong reactivity, making it important to detect in environmental and biological contexts. The additional ions that are being examined are cyanide, magnesium, iron (III), copper, zinc, mercury, and cyanide because of their various effects. Exposure to mercury, especially during pregnancy, can be harmful to development, and the balance between copper and zinc, which are essential for body functioning, must be carefully maintained to prevent poisoning. Consuming iron (III) is necessary, but it should be done so carefully to avoid any potential risks. On the other hand, cyanide exposure and excessive magnesium consumption can have a serious negative impact on health. This review examines the toxicological effects, exposure dangers, and environmental impact of these ions with a focus on their detection and removal. It seeks to emphasise how urgent it is to take preventative action in order to protect ecological stability and human health by implementing effective detection and remediation procedures.

1. Detection of Al^{3+}

We are living in the 'Aluminium Age'. Human exposure to aluminium is inevitable and, perhaps inestimable. Aluminium's free metal cation, $Al^{3+}_{(aq)}$, is highly biologically reactive and biologically available aluminium is non-essential and essentially toxic. So, the detection of Al^{3+} is crucial in biological and environmental sample.

Highly selective and sensitive naphthylamide and iso-quinoline derived fluorescent probe (E)-N'-((2-butyl-6-hydroxy-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-5-yl)methylene)isoquinoline-1-carbohydrazide (NIQ) is synthesized for turn-on fluorescence response for Al^{3+} ion in DMSO/ H_2O solution. Job's plot suggests 1:1 stoichiometry among NIQ and Al^{3+} . The limit of detection is 5.2×10^{-10} M and binding constant 3.27×10^5 M^{-1} . The probe demonstrated successful application for bio imaging Al^{3+} in HeLa cells [1].

Wang, H. *et al.* has reported novel fluorescence sensor (E)-N'-(2-hydroxy-3-methoxybenzylidene)imidazo[2,1-b]thiazole-6-carbohydrazide (L_1) derived from imidazo[2,1,b]thiazole for the detection of Al^{3+} ion in aqueous solution. The probe shows excellent sensitivity and selectivity towards Al^{3+} ion in HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer solution. Limit of detection and binding constant for this ligand and metal ion were calculated around 1.50×10^{-8} M and 7.42×10^4 M^{-1} [2].

Singh, G. *et al.* has reported probe for selective and specific recognition of Al^{3+} , a new Schiff base 4'-((4-(((2-((3-(2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undec-1-yl)propyl)-amino)ethyl)imino)methyl)phenoxy)methyl)[1,1-0-biphenyl]-2-carbonitrile (L_2) functionalized silatrane designed and characterized as potential

chemo-sensor for Al^{3+} ion. From UV and fluorescence spectroscopy demonstrated the receptor's absorption spectrum differs only in the case where the Al^{3+} present in comparison with other ions. The 1:1 stoichiometry confirmed by B-H and Job's plot [3].

Wang, M. *et al.* has reported fluorescent probe tetrastylene derivative (E)-N'-(2-hydroxy-5-(1,2,2-triphenylethyl)benzylidene)isonicotinohydrazide (L_3) synthesized for detection of Al^{3+} ion. Fluorescent properties found by using fluorescence emission spectra due to large conjugated electron effect probe exhibit good AIE at 450-650nm. The stoichiometry of probe to metal ion is 1:1 which is proved by using Job's plot and ESI-MS. Also the probe used to detect the strong acid and alkali as well in living cell imaging [4].

Two novel fluorescence probe 8-hydroxy-N'-(2-hydroxybenzylidene)quinoline-2-carbohydrazide (SQ) synthesized for the detection of Al^{3+} ion by "OFF-ON-OFF" fluorescence response in DMSO- H_2O solution. The interaction mode between probe SQ and Al^{3+} ions was elucidated through fluorescence spectra, UV spectra, HRMS, and NMR titration, revealing the formation of a 1:1 complex involving the ESIPT and CHEF mechanisms. Additionally, DFT calculations supported these findings by simulating electron cloud distribution and energy changes before and after complex

formation. Furthermore, filter paper and cell imaging experiments have showcased the potential practical applications of probes SQ for monitoring Al^{3+} ions in both environmental and in vivo [5].

(N',N''E,N',N''E)-N',N''-(((3-oxo-1,3-dihydroisobenzofuran-1,1-diyl)bis(2-hydroxy-5,1-phenylene))bis(methanylylidene))bis(furan-2-carbohydrazide) (FF2H) a novel phenolphthalein-based Schiff base for the detection of Al^{3+} ion was synthesised. The probe gives "turn-on" response towards the Al^{3+} ion in acetonitrile and HEPES solution. The response towards metal ion is due to CHEF effect which prevents -C=N- isomerism, ESIPT and PET within the probe. The job's plot and 1H -NMR titration confirms the 1:2 stoichiometry [6].

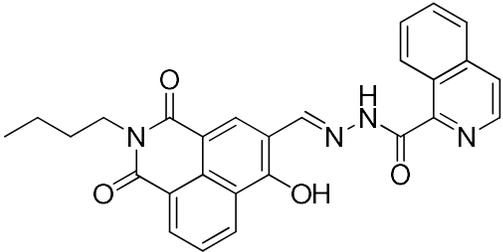
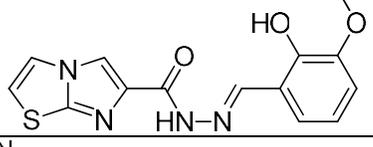
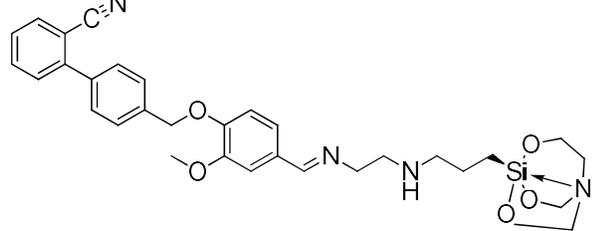
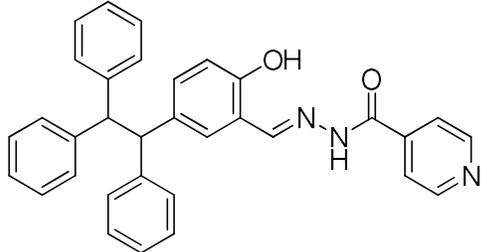
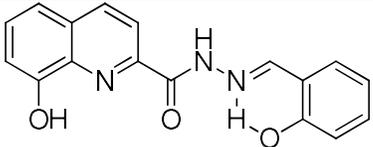
A novel Fluorescent "turn-on" thiophene derived Schiff base (E)-N'-(2,4-dihydroxybenzylidene)thiophene-2-carbohydrazide (PEGSB₁) shows high selectivity and sensitivity in water towards the Al^{3+} with cyan emission. The pH range for detection is around 5-9 pH. Revert detection ability was confirmed by alternate addition of Al^{3+} and EDTA to its aqueous solution which results in construction of an INHIBIT molecular logic gate [7].

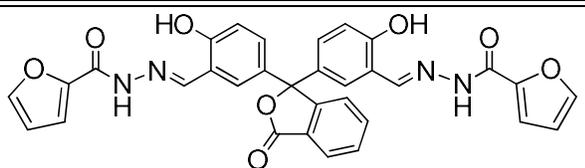
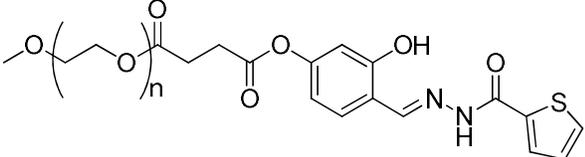
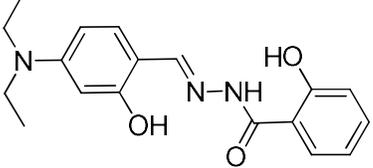
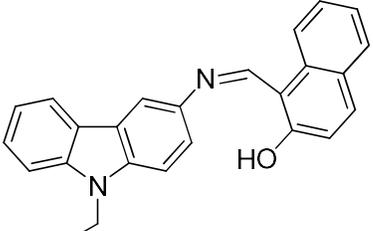
Kumar, M. *et al.* has reported 4-(N,N-Diethylamino)salicylaldehyde derived Schiff base chemosensor (E)-N'-(4-(diethylamino)-2-hydroxybenzylidene)-2-hydroxybenzohydrazide

(H₃L₄) shows high selectivity towards Al³⁺ ion via “turn-on” cyan fluorescence emission at 481nm at saturation point. The stoichiometry of H₃L₄ and metal ion is found 2:1 ratio via job’s plot calculations. The Gibbs free energy of complex calculated around -1272.00 kcal/mol. The optical and electronic properties with help of Time Dependent-Density functional theory (TD-DFT) [8].

For biological imaging in the cell in aqueous-ethanol environment to detect the Al³⁺ by using the fluorescence probe 1-(((9-ethyl-9H-carbazol-3-yl)imino)methyl)naphthalen-2-ol (L₅) derived from 2-hydroxy benzaldehyde and carbazole moieties. The significant fluorescent enhancement is found at the 533nm wavelength. By addition of chelating agent EDTA the ligand-ion complex formation reversed [9] (Table 1).

Table 1: Fluorescent probe for Al³⁺ detection

Compound	Probe Name	Mechanism	$\lambda_{ex}/\lambda_{em}$	LOD
	NIQ	CHEF	510nm	5.2×10 ⁻⁸ M
	L ₁	CHEF	324nm	1.5×10 ⁻⁸ M
	L ₂	ICT	354nm	9.8×10 ⁻⁹ M
	L ₃	AIE	450-650nm	1.587×10 ⁻⁷ M
	SQ	ESIPT	405nm	1.48×10 ⁻⁸ M

	FF2H	CHEF	448nm	$7 \times 10^{-9} \text{M}$
	PEGSB ₁	CHEF	444nm	$1.32 \times 10^{-8} \text{M}$
	H ₃ L ₄	ICT	378nm	$1.2 \times 10^{-6} \text{M}$
	L ₅	CHEF	533nm	$2.59 \times 10^{-7} \text{M}$

1. Detection of Hg²⁺:

Mercury exposure during pregnancy can result in developmental delays and motor skill difficulties in the unborn child. Moreover, mercury released into the environment accumulates in the food chain, contaminating aquatic organisms and posing risks to humans and wildlife through bioaccumulation.

Musikavanhu, B. *et al.* has reported novel Schiff base probe (E)-N-(thiophen-2-ylmethylene)quinolin-8-amine (QT) synthesised from 8-aminoquinoline and thiophene-2-carboxaldehyde. Because of coordination by sulphur and nitrogen ligand undergoes into fluorescence enhanced quenching exposed to

Hg²⁺. The stoichiometry of ligand metal proved by job's plot is 2:1 [10].

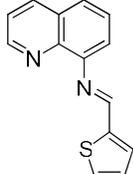
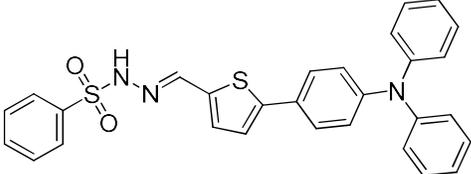
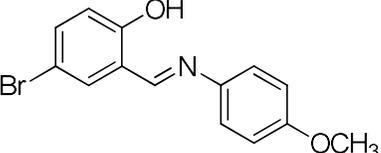
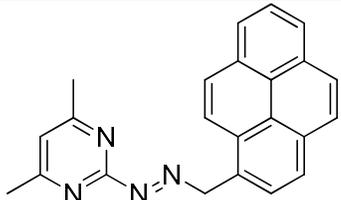
A novel fluorescent Schiff base probe N'-((5-(4-(diphenylamino)phenyl)thiophen-2-yl)methylene)benzenesulfonohydrazide (BS) synthesized for rapid recognition for Hg²⁺ with $2.84 \times 10^{-8} \text{ M}$ detection limit. The probe synthesized using 4-bromotriphenylamine, 5-formaldehyde-thiophene-2-boronic acid and benzenesulfonyl hydrazide and characterized by NMR and HR-MS. The important application of the probe is great reversibility as well as detect Hg²⁺ in water samples which leads to its utilization in molecular logic gate construction. Around 99.93% removal rate of Hg²⁺ by doping BS and polyacrylamide [11].

A new Schiff base 4-bromo-2-[(4-methoxyphenylimino)methyl]phenol (BMPMP) synthesised using 4-bromo-2-[(4-methoxyphenylimino)-methyl]phenol as ionophore and utilized as a neutral carrier to design a new PVC membrane for Hg^{2+} ion. ATR-FTIR spectra using electro de membrane proves Hg^{2+} -BMPMP co-ordination through nitrogen and oxygen. Membrane with composition of 32% polymer (PVC), 2% ionophore (BMPMP), 1.5% ionic additive (NaTPB), and 64.5% plasticizer (o-NPOE) gives optimum response towards Hg^{2+} ion over wide concentration ranges from (0.0933-3980 μM) [12].

Ghosh, S. *et al.* has reported novel Schiff base 2-(4,6-dimethylpyrimidin-2-yl)-1-((pyren-

8-yl)methylene)hydrazine (PYPH) derived from pyrimidine with aim of creating a fluorescent chemical sensor for aqueous Hg^{2+} detection. The characterization of this ligand performed by using UV-vis, FTIR, 1H -NMR and Mass spectroscopy. The chemo sensor displays a turn off fluorescence response towards the Hg^{2+} ion. The selectivity and sensitivity of this ligand examined by spectroscopical approach. Job's plot, HRMS spectral analysis and 1H -NMR analysis confirm the 2:1 binding stoichiometry. Additionally, the ground-state geometry of PYPH was optimized using density functional theory (DFT). These findings indicate that PYPH has promising potential for detecting Hg^{2+} ions in environmental analysis systems [13] (Table 2).

Table 2: Fluorescent probe for Hg^{2+} detection

Probe	Probe Name	Mechanism	$\lambda_{ex}/\lambda_{em}$	LOD
	QT	CHEF	331nm	$2.34 \times 10^{-8} M$
	BS	AIE	549nm	$2.84 \times 10^{-8} M$
	BMPMP	-	-	$3.98 \times 10^{-8} M$
	PYPH	-	398nm	$4.2 \times 10^{-6} M$

2. Detection of Cu²⁺ :

Exposure to copper ions can result in gastrointestinal distress, liver and kidney damage, neurological symptoms, anaemia, skin irritations, and environmental harm. Maintaining a balance of copper intake is crucial for health, while excessive exposure should be minimized and managed, particularly in cases of genetic conditions like Wilson's disease.

Zhang, D. *et al.* has reported 1,2-phenylenediamine-2,6-pyridinedialdehyde (BS-MSB₂) macrocyclic Schiff base, a macrocyclic Schiff base fluorescent probe (in DMSO/H₂O buffer solution pH=6.5) by using 2,6-pyridinedialdehyde was synthesised for detection of Cu²⁺ in living cell imaging and environmental aqueous sample. In EDTA regulation probe shows logic gate behaviour in water samples for Cu²⁺ detection [14].

Tomer, N. *et al.* has reported novel Schiff base probe (E)-N'-((4-oxo-4H-chromen-3-yl)methylene)pyrazine-2-carbohydrazide (L₆) based on chromone synthesised by using 3-formyl-chromone and pyrazine-2-carbohydrazide and characterized by various spectroscopic method like ¹H-NMR, FTIR and HRMS. The probe used to detect Cu²⁺ metal ion by instant colour change from colourless to yellow which is confirmed by UV-visible spectroscopic technique. The binding stoichiometry of Cu²⁺ ions with ligand L₆ was established as 1:1 through Job's plot and HRMS

data. DFT computations supported the proposed binding framework between ligand L₆ and Cu(II) ions. The practical applicability of ligand L₆ was successfully demonstrated in the identification and quantification of Cu²⁺ ions in real water samples [15].

Wang, S. *et al.* has reported polymeric sensor 1,10-Phenanthroline-2,9-dicarboxaldehyde-2,5-diaminoterephthalic acid (PTDA-DATA-SB₃P) a novel fluorescent probe based on Schiff base polymer is synthesised for detection of Cu²⁺ which displays irregular nanosphere of 5µm of diameter. This polymeric fluorescence Schiff base probe synthesised by using 1,10-phennanthroline-2,9-dicarboxaldehyde and 2,5-diaminoterephthalic acid. Characteristic emission peak found at 565 nm. The PDTA group coordinate with Cu²⁺ due to carboxylic group of DATA. Due to PET after addition of metal ion weakened the fluorescence [16].

Goel, A. *et al.* has reported novel Schiff base 4-Hydroxy-6-methyl-3-[1-(2-morpholin-4-yl-ethylimino)-ethyl]-pyran-2-one (DM) based on pyranone can detect the Cu²⁺ ion using UV-Vis absorption, Fluorescence and colorimetric methods. The Schiff base shows colour change pale yellow to colourless by addition of Cu²⁺ ion in UV-Vis absorption band. The stoichiometry of this “turn off” complex of metal ion and DM proved as 1:2 by Job's plot, HR-MS and ¹H-NMR titration data. The probe is not depended to any

pH so there is a no limitation of pH for this probe towards the detection of metal ion [17].

Ghosh, S. *et al.* has reported novel fluorescent probe 3-[(2-hydroxy-naphthalen-1-ylmethylene)-hydrazono]-butan-2-one oxime (NPTH) is used for detection of Cu^{2+} . NPTH and metal ion complex results as non-fluorescent probe. The binding site of this complex has been identified via NMR spectra [18].

(E)-7-hydroxy-4-methyl-8-(((4-(1,2,2-triphenylethyl)phenyl)imino)methyl)-2H-chromen-2-one (CTPE) a novel coumarin and 1-(4'-aminophenyl)-1,2,2-triphenylethene derived Schiff base used as "turn-off" chemosensor for Cu^{2+} detection. Fluorescence of CTPE is rapidly quenched by Cu^{2+} metal ion and it rapidly and selectively distinguish the Cu^{2+} and other metal ion via "turn-off" response [19].

Aniline and naphthalenedialdehyde based Schiff base fluorescent probe 1,5-bis((E)-(phenylimino)methyl)naphthalene-2,6-diol (L_7) with AIEE characteristic was developed for Cu^{2+} detection with "turn-off" phenomenon The 1:2 stoichiometry is proved by UV-Vis / fluorescence titration, job's plot and NMR titration. In presence of Cu^{2+} ion probe shows colour change yellow to brown in day light and bright to dark under UV irradiation [20].

2-(benzo[d]thiazol-2-yl)-6-(((2,4-dimethylphenyl)imino)methyl)phenol (HBTA): Nested fluorescence probe design to overcome the limitation of current fluorescence probes. The

HBTA probe synthesized by utilizing (2-(2-Hydroxyphenyl)-benzothiazole) HBT. The respective probe demonstrate three-stage response towards the Cu^{2+} ion. The hydrolysate (HBT-CHO) showed binding ratio of 2:1 to metal ion. HBT-CHO shows selectivity in detect Cysteine (Cys) by undergoing cyclization with formyl group which leads to change the fluorescent colour change Green to Blue. Based on affinity of Cys to Cu^{2+} metal ion the probe demonstrate logical response where colour change is correlated with concentration of Cu^{2+} and Cys [21].

Slassi, S. *et al.* has reported novel colorimetric and fluorescence chemosensor 2-((Z)-((3-(1H-imidazol-1-yl)propyl)imino)methyl)-6-methoxy-4-((E)-(4-methylphenyl)diazenyl)phenol (SB_4) developed by utilizing 2-hydroxy-3-methoxy-5-((aryl) diazenyl)benzaldehyde and N-(3-aminopropyl)imidazole. The synthesized sensor shows dual mode sensing of Cu^{2+} by colorimetric and fluorimetric method. ICT and CHEF process is responsible for responsive mechanism [22].

Sahu, M. *et al.* has reported novel azine based fluorescent colorimetric sensor [6,6'-((1,10)-hydrazine-1,2-diylidene bis(methanylylidene))bis(2-(6-methoxy)phenol] (H_2L_8) is synthesised for selective and sensitive dual detection of Cu^{2+} metal ion. Presence of Cu^{2+} metal ion identified by UV and Fluorescence spectra by instant colour change

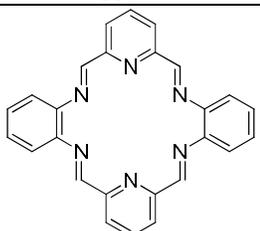
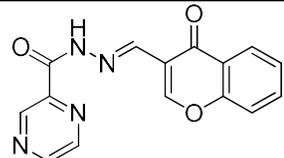
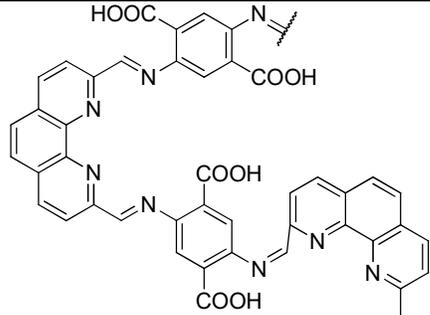
colourless to intense yellow. The probe works at any pH, which leads to use of the respective sensor in detection and quantification of Cu^{2+} in various environmental samples. Also it is used for INHIBIT and IMPLICATION type molecular logic gate [23].

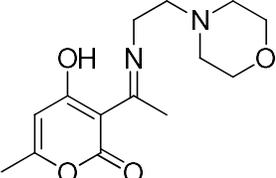
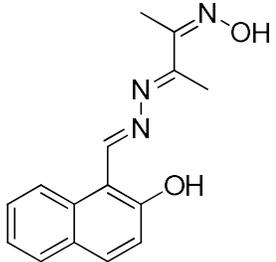
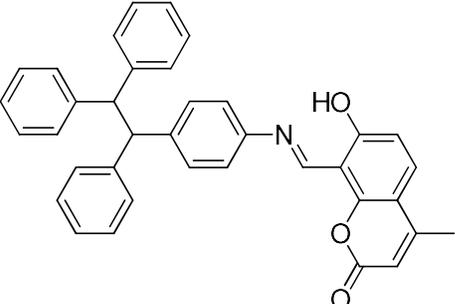
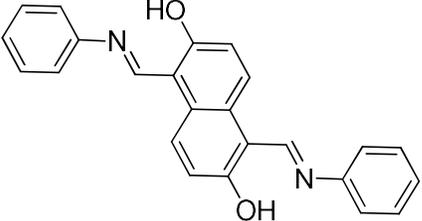
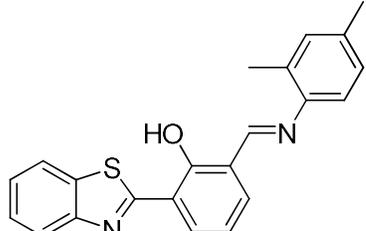
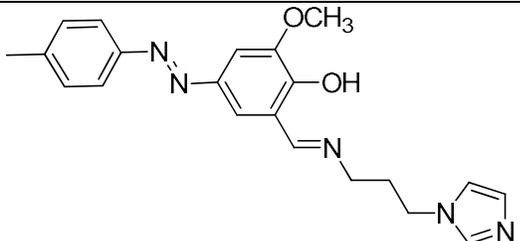
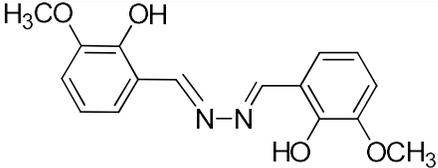
Salih, K. S. *et al.* has reported (E)-4-nitro-2-(((2-(piperazin-1-yl)ethyl)imino)methyl)phenol (NNNOH) tetradentate Schiff Base–functionalized ligand (SB_5) and its complex with Cu^{2+} successfully synthesised and also characterized by spectroscopic methods. The respective metal complex display solatochromic behaviour and also high catalytic activity in selective oxidation

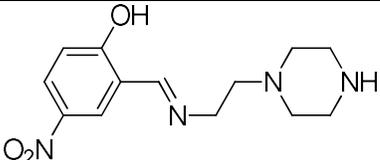
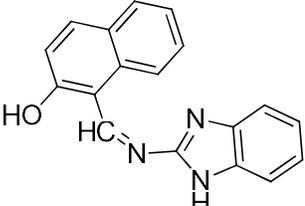
reactions. The complex also hold potential application as optical sensor, Lewis acid-base colour indicator and efficient catalyst [24].

Novel benzimidazole derived fluorescent active Schiff base 1-[[[(1H-1,3-benzodiazol-2-yl)imino] methyl]naphthalen-2-ol (HBN) synthesised and characterized with high selectivity towards Cu^{2+} on on-off-on AIE phenomenon. The probe shows good response towards Cu^{2+} detection at neutral pH in $\text{CH}_3\text{CH}_2\text{OH}$ -PBS solution. Probes effectiveness as solid optical sensor was achieved and exhibit great selectivity and usability for Cu^{2+} metal ion detection when incorporated into paper strip [25] (Table 3).

Table 3: Fluorescent probe for Cu^{2+} detection

Probe	Probe Name	Mechanism	$\lambda_{\text{ex}}/\lambda_{\text{em}}$	LOD
	BS-MSB ₂	-	390nm	$8.33 \times 10^{-9}\text{M}$
	L ₆	ICT	428nm	$3.9 \times 10^{-7}\text{M}$
	PTDA-DATA-SB ₃ P	PET	565nm	$1.15 \times 10^{-9}\text{M}$

	DM	CHEF	439nm	7.7nM 7.7×10⁻⁹M
	NPTH	-	398nm	4.11×10⁻⁴M
	CTPE	AIE	565nm	0.36×10⁻⁴M
	L7	AIEE	565nm	1.64×10⁻⁸M
	HBTA	ESPIT	350nm	5.4×10⁻⁶M
	SB4	CHEF/ICT	286nm	0.6×10⁻⁶M
	H2L8	CHEF	360nm	3.8×10⁻⁸M

	SBs	LMCT	475nm	$3.8 \times 10^{-8} \text{M}$
	HBN	AIE	365nm	$8.14 \times 10^{-8} \text{M}$

3. Detection for Zn^{2+} :

Zinc metal ions can result in gastrointestinal distress, respiratory issues, neurological symptoms, immune system disruption, and skin irritation. While zinc is essential for health, maintaining a proper balance of intake is crucial to prevent toxicity. This is particularly important in occupational settings and when considering dietary supplementation. Environmental discharge of zinc should also be monitored to prevent harm to aquatic ecosystems.

Wang, J. T. *et al.* has reported Quinoline-2-carboxyaldehyde-(pyridine-2-carbonyl)-hydrazide (QCPCH) synthesized for rapid (less than 3s) for detection of Zn^{2+} . The detection of QCPCH towards Zn^{2+} based on combined CHEF and inhibiting PET phenomenon. The fluorescent chemosensor can able to detect Zn^{2+} in water samples and also used in qualitative and quantitative determination of Zn^{2+} by made into test strip [26].

A novel fluorescent Schiff base (E)-N'-(2-hydroxynaphthalen-1-yl)methylene) furan-2-carbohydrazide (NFC) synthesized from 2-hydroxy-naphthaldehyde formaldehyde and furan-2-carbohydrazide. This fluorescence probe used to detect the Zn^{2+} in water medium and the cell fluorescence imaging experiment reveals that the probe has capability to trace Zn^{2+} within living cell with minimal harm to cell health [27].

Muthusamy, S. *et al.* has reported novel star-shaped Schiff base triaminoguanidine-thiophene based fluorophore tris((E)-2-(thiophen-2-yl)methylene)hydrazinyl)methane (TAT) was designed for the sequential detection of Zn^{2+} and citrate within mitochondria. TAT initially emits yellow fluorescence upon the addition of Zn^{2+} via an ICT mechanism and subsequently forms a TAT- Zn^{2+} complex that chelates with citrate, resulting in a ratiometrically enhanced red emission at 692 nm through an AIE mechanism. This innovative non-IDA-type approach for citrate sensing using a metal

complex offers a novel pathway for detecting anions. The successful yellow and red emission signals of TAT for Zn^{2+} and citrate were demonstrated via paper-based test strips and further validated through in vitro and in vivo experiments using PC3 living cells and mice. The bio imaging results show TAT's ability to target mitochondria and distinguish cancerous from non-cancerous prostate cells. TAT's excellent sensing performance in various settings suggests its potential application in prostate cancer diagnosis, serving as a prototype for point-of-care detection tools in clinical practice [28].

By using AIE and ESIPT phenomenon a multifunctional tetraphenylethene based Schiff base 2-((E)-((2-((E)-(2-hydroxy-4-(1,2,2-triphenylvinyl)benzylidene)amino)phenyl)imino)methyl)-4-(1,2,2-triphenylvinyl)phenol (TPESB₆) synthesised. The respective Schiff base exhibit remarkable absorption/fluorescence dual-mode colour changes which triggered by water and Zn^{2+} ion. Also exhibits low cytotoxicity and successfully shows effectiveness in Zn^{2+} sensing within the living cell, as well as it is used in eco-friendly inkless rewritable paper and also used in information security and anti-counterfeiting [29].

Coumarin based 2-((7-hydroxy-4-methyl-2-oxo-2H-chromen-8-yl)methyleneamino)-3-phenyl- propanoate (FS3) fluorescence probe is synthesized and probe exhibit fluorescence quenching towards the Zn^{2+} ion. By using EDTA

chealator probe exhibit a good reversibility. By fluorescence microscope it was found that probe has no toxic effect towards L929 cell by MTT method [30].

Theetharappan, M., & Neelakantan, M. A. has reported o-vanillin and DL-2,3-diaminopropionic acid derived water soluble Schiff base 2,3-bis((E)-(2-hydroxy-3-methoxybenzylidene)amino)propanoic acid (ODA) synthesised, and evaluated as turn-on chemosensor. The Chromogenic response visible to naked eye in exposure of Zn^{2+} . The sensing mechanism is due to inhibition of ESIPT and isomerization of -C=N- of probe on complexation. The fluorescence sensing ability leads to potential biological application detect by live cell imaging of this probe towards human glioblastoma U87 and hepatoma C3A cancer cell for Zn^{2+} detection [31].

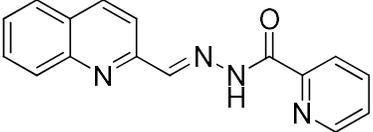
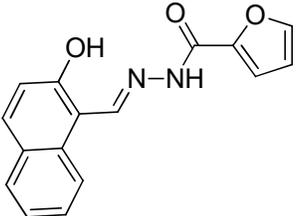
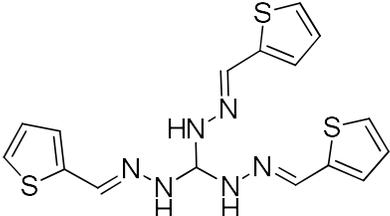
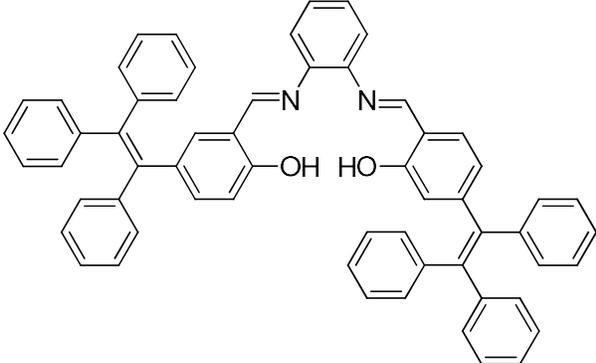
A Chiral polyamine macrocycle Schiff Base (C-1) design derived from diformyl-bisbinaphthyl and o-phenylenediamine. By adding Zn^{2+} the probe shows "turn-on" response backed with enhancement in enhancement at 510nm for Zn^{2+} [32].

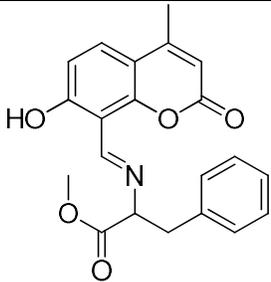
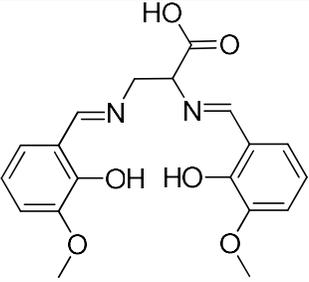
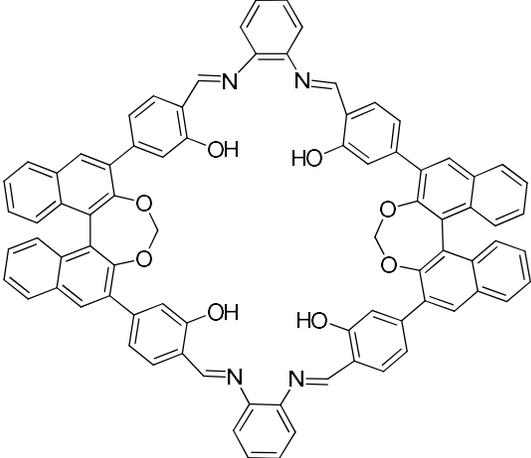
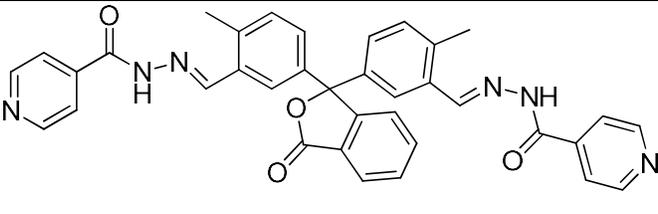
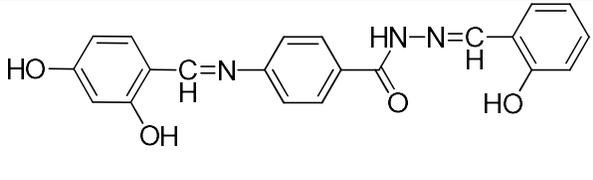
(N',N'''E,N',N'''E)-N',N'''-(((3-oxo-1,3-dihydroisobenzofuran-1,1-diyl)bis(2-methyl-5,1-phenylene))bis(methanylylidene))di(isonicotino hydrazide) (FFIZNA) phenolphthalein derived fluorogenic probe synthesised for monitor Zn^{2+} via turn-on response [33].

4-((2,4-dihydroxybenzylidene)amino)-N'-(2-hydroxybenzylidene)benzohydrazide (P₁) fluorescent probe for detecting aqueous Zn²⁺ ions were synthesized. These probes incorporated salicylaldehyde benzoyl hydrazine as a recognition group and -C=N- as the distinctive fluorescence chromophore. Spectroscopic examinations, primarily fluorescence spectroscopy (FS), demonstrated the probes' exceptional selectivity for Zn²⁺ ions compared to

other metal ions. This selectivity remained stable across a wide pH range from 6.0 to 9.0. Furthermore, assessments of cytotoxicity and fluorescence imaging in ECV304 cells revealed the probes' rapid response and ability to penetrate cell membranes. These findings suggest promising future applications for these probes in clinical Zn²⁺ detection and the dynamic analysis of Zn²⁺ in biological systems [34] (Table 4).

Table 4: Fluorescent probe for Zn²⁺ detection

Probe	Probe Name	Mechanism	$\lambda_{ex}/\lambda_{em}$	LOD
	QCPCH	CHEF	484nm	7.2×10 ⁻⁸ M
	NFC	PET	428nm	1.18×10 ⁻⁸ M
	TAT	ICT/AIE	692nm	1.02×10 ⁻⁸ M
	TPESB ₆	AIE/ESIPT MV	-	38.9×10 ⁻⁸ M

	FS3	-	350nm	$3.43 \times 10^{-9} \text{M}$
	ODA	ESIPT	350nm	$7.06 \times 10^{-9} \text{M}$
	C-1	LMCT	510 nm	$1 \times 10^{-5} \text{M}$
	FFIZNA	CHEF	494nm	$4.21 \times 10^{-9} \text{M}$
	P ₁	FRET	536nm	-

4. Detection of Fe³⁺ :

Iron (III) ions are not typically hazardous in the context of essential nutrient intake, excessive exposure to iron, such as through

accidental ingestion of iron supplements or industrial settings, can lead to various health risks. These risks include gastrointestinal distress, iron poisoning (especially in children),

the development of hemochromatosis, oxidative stress, neurological effects, and potential organ damage. Careful handling of iron supplements, proper storage to prevent accidental ingestion, and medical supervision when using iron supplements are crucial measures to mitigate these hazardous effects.

N0-(3-ethoxy-2-hydroxybenzylidene)-4,5-dihydronaphtho[1,2-b]thiophene-2-carbohydrazide (LB2), A novel Schiff base fluorescent sensor derived from 4,5-dihydronaphtho[1,2-b]thiophene-2-carbohydrazide and 3-ethoxy-2-hydroxybenzaldehyde. In DMF-H₂O buffer it can detect the In²⁺ and the resultant complex [LB2+In] can detect the Fe³⁺ which proven by fluorescence titration in [tris(hydroxymethyl)aminomethane] buffer solution. The response of detection will be “off-on-off” [35].

1-phenyl-3-ferrocenyl-enone-aminourea Schiff base probe (M1) a straightforward sensor was synthesised from 1-phenyl-3-ferrocenone and aminourea by solvent free method. The probe shows excellent selectivity towards the Fe³⁺ ion in methanol. The complexation ratio of probe and metal ion is 2:3 by job's plot curve analysis. Complexation constant of probe with metal ion is $4.001 \times 10^4 \text{ M}^{-1}$ found by benesi-hildebrand equation. The sensor exhibited an ideal pH range between 6 and 8 and retained its impressive ion detection capabilities within 0-80 minutes and

even after a 24-hour duration, rendering it well-suited for practical use. Significantly, our newly created sensor can serve as an efficient test strip for identifying Fe³⁺ ions [36].

Two novel schiff base potassium (E)-2-((2-hydroxy-3-methoxybenzylidene)amino)acetate (L₉) and its complex [Zn₂(*o*-van-gly)(phen)OAc)₂].3MeOH (1) and [Cu(*o*-van-gly)(bipy)].MeOH (2) synthesised and their crystal structures characterized by single-crystal XRD. The complex 1 shows selectivity and sensitivity towards detection of Fe³⁺ ion. Also both complexes displayed strong anti-cancer effects against four different human cancer cell lines, indicating their promise as potential novel anti-cancer agents [37].

Water soluble Schiff base Sodium(E)-2-amino-5-((2-hydroxybenzylidene)amino)-benzene-sulfonate (L₁₀) derived from salisaldehyde and 2,5-diaminobenzenesulfonic acid and characterized by ¹H-NMR, single-crystal X-ray analysis and Mass spectroscopy. An analysis of its electronic absorption and fluorescence characteristics unveiled noticeable differences in spectral patterns across various solvents. In water, a noteworthy emission peak at 430 nm was observed. Impressively, the compound displayed high sensitivity and specificity for detecting Fe³⁺ ions, boasting a low detection limit of $1.29 \times 10^{-6} \text{ M}$ [38].

Jothi, D. *et al.* has reported novel Schiff base probe (E)-6-((4-(diethylamino)-2-hydroxybenzylidene)amino)-2-(2-morpholinoethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (NDSM) synthesised and used for the detection of Fe^{3+} ion by fluorimetric method. NDSM exhibited a substantial increase in absorbance at 360 nm and a visible color change to golden yellow in acetonitrile:water (7:3, v/v) medium in the presence of Fe^{3+} ions. The fluorescence emission intensity at 531 nm was significantly quenched by Fe^{3+} ions, with minimal interference from other ions. NDSM also displayed lysosome target ability due to its morpholine unit. The reversible fluorescence response to Fe^{3+} ions was confirmed using the complexing agent EDTA. The real-time applicability of NDSM for Fe^{3+} detection was demonstrated in various scenarios, including test paper-based detection, molecular logic gate construction, quantification in water samples, and fluorescence imaging of Fe^{3+} [39].

A novel tris(4-formylphenyl) amine and a chiral hydrazide precursor covalent organic framework synthesised having hydrazone linkage by utilizing tris(4-formylphenyl)amine and chiral hydrazide precursor. The particular covalent organic framework work as a highly selective and sensitive fluorescence sensor for Fe^{3+} detection in ethanol. A uniform Tfpa-Mth co-ordination framework film of uniform thickness attached to

QCM chip results Fe^{3+} detection in real-time with high selectivity [40].

Kaur, S. *et al.* has reported 1,1'-((ethane-1,2-diylbis(oxy))bis(2,1-phenylene))bis(N-p-tolylmethanimine) (SB₇) a novel Schiff base ionophore was synthesized and utilized for the highly specific detection of Fe^{3+} ions using voltammetry and potentiometry, achieving remarkably low detection limits. UV-Visible and fluorescence measurement confirmed the binding interaction of probe and metal ion. When applied to real sample matrices like surface water, groundwater, and pharmaceutical tablets, carbon paste electrode CPE-SB₇ demonstrated precision and accuracy. This approach has the potential to assess Fe^{3+} content in diverse samples, encompassing food crops, biological specimens (blood, urine), and environmental samples (water, soil) [41].

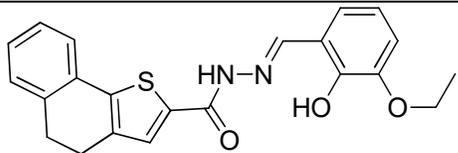
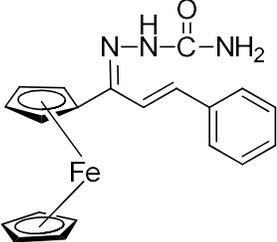
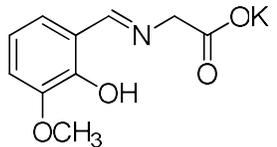
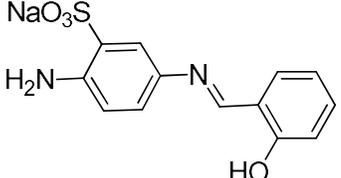
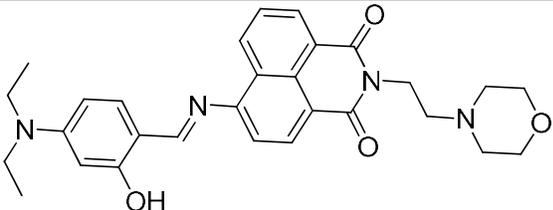
A novel fluorescent probe 1-(3-(7-(diethylamino)-2H-chromen-3-yl)-5-(4-(diphenylamino)phenyl)-4,5-dihydro-1H-pyrazol-1-yl)ethanone (A) based on coumarin-pyrazoline synthesised and characterized by using ¹H-NMR, ¹³C-NMR and HR-ESI MS and optical properties characterised by UV-Vis absorption and fluorescence emission spectra which shows reduction in fluorescence intensity in presence of Fe^{3+} . The reduction fluorescence intensity and Fe^{3+} concentration shows linear relationship. The probe could be easily restored to its original state by adding EDTA. Also the

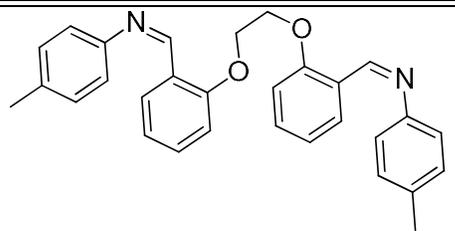
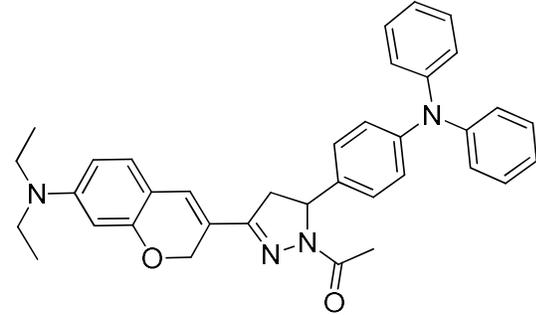
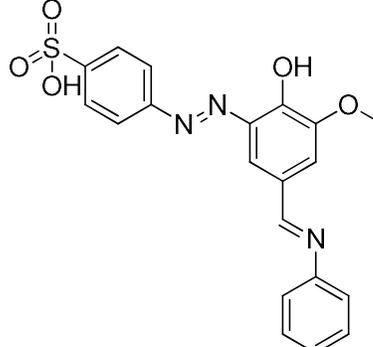
probe proved to be useful for practical cell imaging applications [42].

Priyanga, K. T. A. *et al.* has reported A novel fluorescent chemosensor 4-((E)-(2-hydroxy-3-methoxy-5-((E)(phenylimino)methyl)phenyl)diazetyl)benzene sulfonic acid (L₁₁) was synthesised containing imine group together with the azo functional groups because of that it can applicable for Fe³⁺ sensing. Job's plot and the Benesi-Hildebrand

equation revealed the formation of a 1:1 complex between L₁₁ and Fe³⁺ ions, with an association constant of $1.56 \times 10^4 \text{ M}^{-1}$. The interference tests affirmed L₁₁'s ability to detect Fe³⁺ ions without being significantly affected by other metal ions, making it a promising water-soluble and selective fluorescent chemosensor for Fe³⁺ ions, especially in real-time water monitoring applications [43] (Table 5).

Table 5: Fluorescent probe for Fe³⁺ detection

Probe	Probe Name	Mechanism	$\lambda_{ex}/\lambda_{em}$	LOD
	LB ₂	LMCT	516nm	$2.59 \times 10^{-8} \text{ M}$
	M ₁	PET	450nm	$6.92 \times 10^{-7} \text{ M}$
	L ₉	-	540nm	-
	L ₁₀	AIEE	430nm	$1.29 \times 10^{-6} \text{ M}$
	NDSM	ICT	531nm	$8 \times 10^{-7} \text{ M}$
Tfpa-Mth COF	Tfpa-Mth COF	-	360nm	$6.4 \times 10^{-8} \text{ M}$

	SB ₂	ICT/LMCT	531nm	0.8×10 ⁻⁶ M
	A	-	523nm	1.01×10 ⁻⁷ M
	L ₁₁	LMCT/PET	341nm	0.31×10 ⁻⁶ M

5. Detection of Mg²⁺ :

Mg²⁺ are essential for normal body functions and are generally safe when obtained from a balanced diet. However, excessive magnesium intake, especially from supplements or in individuals with kidney issues, can lead to various hazardous effects. These effects include gastrointestinal disturbances, kidney damage, muscle weakness, cardiac and respiratory complications, hypotension, and neurological symptoms. Therefore, it is essential to use magnesium supplements cautiously, under medical guidance, and to be aware of the potential risks associated with excessive

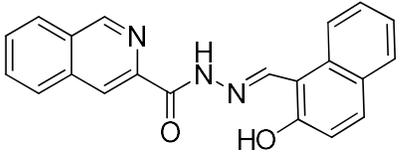
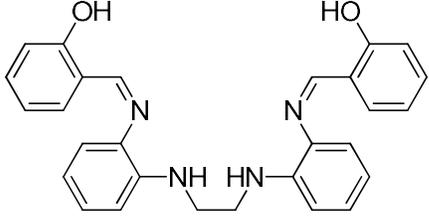
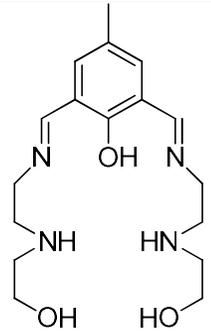
magnesium intake, particularly in vulnerable populations.

A novel fluorescence probe N'-((1-hydroxynaphthalen-2-yl)methylene)isoquinoline-3-carbohydrazide (NHMI) shows turn-on fluorescence towards Mg²⁺ with detection limit of 1.20×10⁻⁸ M. The naked eye detection is responsible because of PET, ESIPT and CHEF effect. The probe is formed by using isoquinoline-3-carbohydrazide and 2-hydroxy-1-naphthaldehyde. The absorption band of probe is found at 370nm but the metal ligand binding shift the band at 439nm [44].

Azadbakht, R. *et al.* has reported A new naphthol based weak fluorescent Schiff base 2,2'-((1Z,1'Z)-(((ethane-1,2-diylbis(azanediyl))bis(2,1-phenylene))bis(azanylylidene))bis(methanylylidene))diphenol (H₂L₁₂) synthesised which is used for the detection of Mg²⁺ ion. The probe shows weak fluorescence (f = 0.031) which enhances by adding the Mg²⁺ ion (f=0.182). The fluorescence enhancement is due to PET and -C=N-isomerization phenomenon. Because of the fluorescence enhancement the probe is used for construction of molecular logic gate INHIBIT by using Mg²⁺ as input [45].

Chattopadhyay, K. *et al.* has reported A novel fluorescence sensor 2,2'-(((1E,1'E)-((2-hydroxy-5-methyl-1,3-phenylene)bis(methanylylidene))bis(azanylylidene))bis(ethane-2,1-diyl))bis(azanediyl))diethanol (H₃L₁₃) based on amino-phenol-alcohol was constructed by using 2,6-bis{2-(2-hydroxyethylamino)ethylimino}methyl-4-methylphenol act as a fluorescence sensor for Mg²⁺ ion sensing via CHEF phenomena. After the observation it is also found that the ligand H₃L₁₃ and H₃L₁₃-Mg²⁺ complex can readily use for cellular application at specific dose and time of incubation because they are not cytotoxic [46] (Table 6).

Table 6: Fluorescent probe for Mg²⁺ detection

Probe	Probe Name	Mechanism	$\lambda_{ex}/\lambda_{em}$	LOD
	NHMI	PET/ESPIT/CHEF	415nm	7.69×10 ⁻⁸ M
	H ₂ L ₁₂	PET	490 nm	3.04×10 ⁻⁹ M
	H ₃ L ₁₃	-	442nm	0.86×10 ⁻⁶ M

6. Detection of CN⁻:

CN⁻ is extremely toxic and poses significant hazards to human health and the environment. Its ability to disrupt cellular respiration, leading to acute symptoms such as rapid breathing, confusion, and even death, underscores the urgency of cyanide poisoning treatment. Additionally, cyanide's role in industrial accidents and potential environmental contamination necessitate strict safety measures and regulations to mitigate its risks. Given its potent toxicity, cyanide exposure requires immediate medical attention, making awareness, prevention, and emergency response crucial aspects in managing the hazards associated with cyanide ions.

A novel Schiff base ligand 2,2'-((1E,1'E)-((5-(tert-butyl)-2-hydroxy-1,3-phenylene)bis(methanylylidene))bis(azanylylidene))bis(4-nitrophenol) (KP1) was synthesised by using 2,6-diformyl-4-tert-butylphenol and 2-amino-4-nitrophenol and characterised by various spectroscopic technique. The ligand selective and sensitive detection of CN⁻ ion in DMSO-H₂O medium. The detection mechanism involves deprotonation of phenolic –OH groups which followed by nucleophilic addition to the Carbon atom of imine group. The probes' fluorescence responses are influenced by intramolecular charge transfer (ICT) [47].

Parhegani, F. *et al.* has reported A novel Schiff base CSAN was synthesised by using azo-

derivative of 1-naphthylamine and chitosan. The synthesised probe characterized by using FT-IR, ¹H NMR, UV–Vis, XRD, TGA, and SEM. CSAN proved to be a promising sensor for CN⁻ anions in aqueous media, displaying a noticeable colour change from colourless to pale yellow, along with quantitative chemical analysis [48].

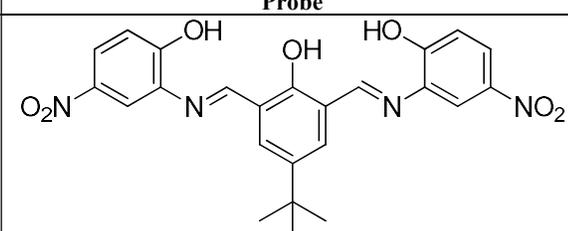
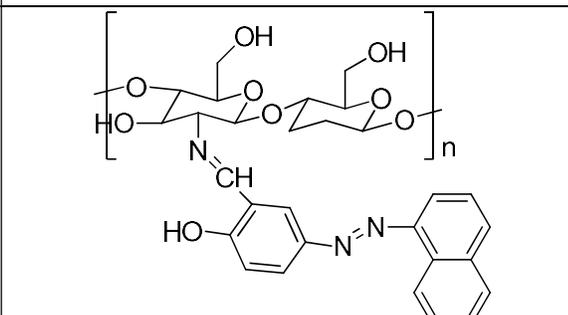
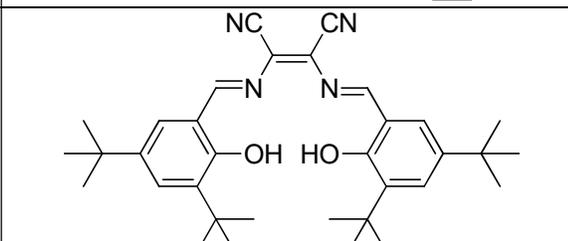
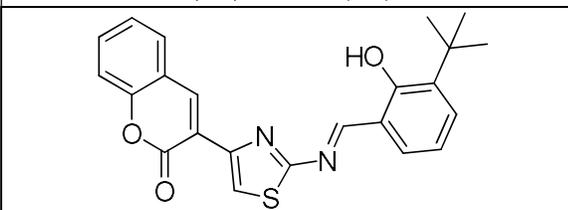
Venkatesan, V. *et al.* has reported A novel Schiff base 2,3-bis((E)-(3,5-di-tert-butyl-2-hydroxybenzylidene)amino)maleonitrile (L₁₄) synthesised by using diaminomaleonitrile with 3,5-tert-butyl-2-hydroxybenzaldehyde and characterized by various spectroscopic techniques. It was observed that probe changes colour from yellow to colourless through visual and UV-Vis techniques. Ligand forms 1:1 complexes with this analyte and operates effectively in the pH range 5–8 for CN⁻ without interference from other competing ions. The binding mechanism between L₁₄ and Zn²⁺ was characterized using ¹H-NMR, ESI mass spectrometry, and DFT analysis. Probe L₁₄ demonstrates promising potential for the detection of CN⁻ in semi-aqueous environments [49].

Şahin, Ö. *Et al.* has reported A novel schiff base ligand (E)-3-(2-((3-(tert-butyl)-2-hydroxybenzylidene)amino)thiazol-4-yl)-2H-chromen-2-one (CTS) synthesised by combining coumarin and thiazole with 3-tertiarybutylsalicylaldehyde and characterised by using ¹H-NMR, ¹³C-NMR, FT-IR and LC-MS

and the photophysical properties of the ligand reveals its sensitivity to CN⁻. Molecular docking studies were conducted to evaluate how the ligand CTS and its metal complexes interact with enzymes, namely cholinesterase (AChE and BChE) and pancreatic cholesterol esterase

(CEase). Both experimental (in vitro) and computational (in silico) findings demonstrated that all of the compounds had significant inhibitory effects on these enzymes [50] (Table 7).

Table 7: Fluorescent probe for CN⁻ detection

Probe	Probe Name	Mechanism	$\lambda_{ex}/\lambda_{em}$	LOD
	KP1	ICT	522nm	$1.7 \times 10^{-7} \text{M}$
	CSAN	-	-	$9.1 \times 10^{-6} \text{M}$
	L11	ICT	424nm	$3.3 \times 10^{-7} \text{M}$
	CTS	ICT	396nm	-

CONCLUSION

This review thoroughly explores a variety of fluorescent probes that were created especially to detect a range of metal ions, such as Al³⁺, Hg²⁺,

Cu²⁺, Zn²⁺, Fe³⁺, Mg²⁺, and CN⁻. Among these ions, a pattern of variable stoichiometry appears, typically indicating a 1:1 or 1:2 relationship, indicating the specificity of these

probes. Additionally, the probes demonstrate remarkable sensitivity, with detection limits ranging from 3.04×10^{-9} M for Mg^{2+} to 1.71×10^{-7} M for CN^- . The clever utilisation of various mechanisms, such as CHEF, ICT, AIE, ESIPT, LMCT, AIEE, and PET, emphasises the design versatility and allows these probes to operate in a variety of pH ranges, typically from 5 to 9 and some of them working at all pH.

Notably, a number of probes exhibit the exceptional capability of functioning as logic gates, highlighting their promise in analytical applications. Each metal ion presents distinct detection limits, with significant emphasis on -OH functional groups for Hg^{2+} , Zn^{2+} , and Mg^{2+} . The review also highlights the usefulness of these probes, especially for Hg^{2+} , where their reversibility of binding increases the amount of mercury ions they can remove. The review highlights the tremendous potential of these fluorescent probes overall, providing a viable path for accurate and effective detection throughout a range of metal ions with different stoichiometry, sensitivity, and useful applications.

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