Water-soluble optical sensors: keys to detect aluminium in biological environment

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Metal ion plays a critical role from enzyme catalysis to cellular health and functions. The concentration of metal ions in a living system is highly regulated. Among the biologically relevant metal ions, the role and toxicity of aluminium in specific biological functions have been getting significant attention in recent years. The interaction of aluminium and the living system is unavoidable due to its high earth crust abundance, and the long-term exposure to aluminium can be fatal for life. The adverse Al^{3+} toxicity effects in humans result in various diseases ranging from cancers to neurogenetic disorders. Several Al^{3+} ions sensors have been developed over the past decades using the optical responses of synthesized molecules. However, only limited numbers of water-soluble optical sensors have been reported so far. In this review, we have confined our discussion to water-soluble Al^{3+} ions detection using optical methods and their utility for live-cell imaging and real-life application.
1. Introduction

The history of humans and metals goes back to centuries, both physiologically and economically, as most of metals have played a significant role in the progress of civilization. Aluminium, being the most abundant metal and the third most element on Earth (8.1% of Earth’s mass), is widely used in our daily life, starting from medicines to aircraft. The presence of non-essential aluminium in life forms leaves the question of toxicity in biological systems. Rigorous research in this field has revealed that aluminium exposure and intake is detrimental to plants, model organisms, and humans (Fig. 1).

Aluminium exists in different forms, such as minerals (aluminium oxides and aluminosilicates), as well as organic and inorganic precipitates, making it an essential component of mineral soil. Though naturally occurring silicates and oxides are harmless, soil acidification due to acid rain and anthropogenic actions can trigger the leaching of aluminium, leading to damage to the growth of plants. The phytotoxicity of Al\(^{3+}\) includes root growth inhibition, reduced crop yield, cell wall damage, plasma membrane disruption, signalling pathway interruption, and nutrient imbalance. Aluminium is easily accessible to both animal and human populations through the inhalation of particles and aerosols, ingestion of food and water, medications, vaccinations, skin contact, dialysis, and infusions. Recent research in neurobiology has revealed that aluminium could act as a neurotoxin, damaging the nerve tissues, which is associated with several neurogenetic disorders such as Alzheimer’s disease, Parkinson’s disease, autism, and multiple sclerosis. Chronic exposure to aluminium to the model organism Caenorhabditis elegans led to the disruption of metallostasis, oxidative stress, premature aging, and sterility. Kamalov et al. reported that an environmentally relevant concentration of aluminium could damage the thymocytes and lymphocytes and gradually the immune system in mice. The adverse effects of aluminium urge the detailed investigation on the detection, selective removal, or conversion of Al\(^{3+}\) to nontoxic species, which are highly necessary to control its concentration below the ecotoxic levels in the biosphere.

To date, a variety of techniques such as inductively coupled plasma emission spectroscopy (ICPES), atomic fluorescence spectroscopy (AFS), and X-ray photoelectron spectrometry (XPS)
have been developed for Al\(^{3+}\) sensing. Despite their high sensitivity and selectivity, complicated instrumentation, high cost, and tricky operation have hindered their practical utility. In this scenario, the development of fluorescent probe-based chemosensors is an active research field that has garnered tremendous momentum over the past few years.\(^{21-36}\) The use of optical probes is considered as the most convenient, inexpensive, effective, and rapid method for the detection of Al\(^{3+}\). Several probes based on rhodamine,\(^{27-28}\) naphthol,\(^{29}\) fluorescein,\(^{30}\) and spirobenzopyran\(^{31}\) have been synthesized to detect Al\(^{3+}\) cations exploiting their color and fluorescence properties. Recently, Prof. Roy has comprehensively reviewed aluminium sensors derived from 2-hydroxy-1-naphthaldehyde, salicylaldehyde, rhodamine, coumarin, and different metal based-metal–organic frameworks (MOFs).\(^{32}\) However, most of the reported chemosensors require mixed aqueous–organic solvent systems due to their poor solubility in polar buffered/aqueous medium. Besides their poor solubility in water, many fluorescent sensors are being used to detect Al\(^{3+}\) in live cells, Drosophila melanogaster, Escherichia coli, zebrafish, rice seedlings, etc.\(^{33-39}\) However, the utilization of organic solvents for cellular imaging can destroy the cells, causing inaccurate sensing of intracellular Al\(^{3+}\). Therefore, the development of water-soluble fluorescent Al\(^{3+}\) sensors would effectively enhance the efficiency of detection to the next level.

In this review, we will attempt to provide a clear picture on different classes of water-soluble aluminium sensing probes based on colorimetric and fluorometric detection (Fig. 2 and Table 1). We limit our discussion to optical sensors that can act in aqueous solutions with organic solvents less than 2%. Rather than focusing on the synthetic ways, we have discussed the efficiency, spectroscopic properties, and practical applications, deeply examined the sensing mechanisms, compared the selectivity, and detection levels of several probes, and highlight the characteristic requirements of a bio-applicable aluminium detecting fluorescent probe.

2. Results and discussions

2.1 Naphthyl-based sensors

From the historical viewpoint, the ultra-sensitive determination of Al\(^{3+}\) through naphthalene derivative dates to 1994.\(^{40}\) Over the years, the endeavor of organic synthesis judiciously tailored naphthalene into numerous fluorogenic molecular architectures for metal sensing. 2-Hydroxy-1-naphthaldehyde or 1-hydroxy-2-naphthaldehyde (HN) is a vastly explored derivative of naphthalene, and has poor quantum yield, shorter fluorescence lifetime,\(^{41}\) and lower cost.\(^{42}\) In addition, successful condensation with appropriate amines afforded Schiff-bases, where the imine nitrogen and naphthal hydroxy behave as hard donors to efficiently coordinate the hard acid Al\(^{3+}\).\(^{43,44}\) Also, the rational choice of amine counterparts can alter the binding sites to furnish strong interaction with the aluminium ion. The distinguished selective chelation with Al\(^{3+}\) augmented the fluorescence intensity of weakly emissive imine chemosensors. Mechanistically, it involves arresting the photoinduced electron transfer (PET) process and isomerization around the C==N bond, exhibiting a chelation enhanced fluorescence (CHEF) effect. Therefore, elegantly developed NH-derived Schiff-bases emerged as promising sensors for Al\(^{3+}\) recognition. Herein, we are dealing with some pertinent examples of this category.

In 1994, Baksi and coworkers employed chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulfonic acid; 1, Scheme 1) as an ultra-sensitive fluorometric reagent for the selective recognition of Al\(^{3+}\) in nano-trace levels.\(^{45}\) The presence of donor-acceptor moieties at 1,6-position made the probe fluorescent. However, discrepancies related to the absence of wide-range studies on the increase in emission intensity with Al\(^{3+}\) ion, binding stoichiometry, and use of acetic acid/acetate buffer (pH = 4.0) made Bardez and coworkers revisit the sensing properties of 1 in 2004.\(^{45}\) An increase in absorption at 360 nm (Fig. 3a) and a fluorescence enhancement at 387 nm (Fig. 3b) was observed upon Al\(^{3+}\) addition. A detailed study by the authors complemented the previous reports on 1 by forming a 1 : 1 complex with a limit of detection of 0.65 µg L\(^{-1}\) at pH = 4.0. They have also demonstrated the application of the probe in determining the Al\(^{3+}\) in different tap water samples. The obtained results were compared with the outcomes attained from the atomic absorption spectroscopy (AAS). However, the methodology is not selective to Al\(^{3+}\), when the interfering ion is Ga\(^{3+}\).

Later, in 2012, Chattopadhyay and coworkers illustrated an efficient dual-mode sensing of Al\(^{3+}\) through colorimetric and fluorescence turn-on behavior of chemosensor 2 (Scheme 1) in HEPES buffer (DMSO/water: 1/100) of pH 7.4.\(^{46}\) The synthesized Schiff-base probe 2 comprises a naphthalene unit behaving as a signalling moiety, whereas the functional groups – hydroxyl and imine provoke the chelating site for the selective binding of Al\(^{3+}\). The complexation of the probe with Al\(^{3+}\) rendered a decrease in the absorbance at 335 and 392 nm with concomitant enhanced absorption at 412 nm (Fig. 3c). The remarkable changes in the absorption spectra facilitated a visible color change of the solution from yellow to reddish-yellow, providing naked-eye detection (Fig. 3c; inset image).
| Sensor | Detection method | Solvent | Wavelength/nm | LOD | K/M⁻¹ | Stoichiometry⁹ | Applications | Reference |
|--------|-----------------|---------|---------------|-----|--------|---------------|--------------|-----------|
| Naphthyl based sensors | Fluorometric | Water (pH 4.0) | 360, 387 | 0.65 μg L⁻¹ | — | 1 : 1 | Water samples | 40, 45 |
| | Fluorometric & colorimetric | HEPES buffer (pH 7.4) (water/DMSO 100 : 1) | 355, 470 | 0.603 μM | 3.5 × 10⁻⁵ | 1 : 1 | Live-cell imaging (HeLa cells) | 46 |
| | Fluorometric & colorimetric | Water | 450, 490/495 | 1 μM | 3.148 × 10⁻⁴ | 1 : 1 | — | 47 |
| | Fluorometric | Bis-tris buffer (pH 7.0) | 450, 490/515 | 0.13 μM | 2.5 × 10⁻³ | 1 : 1 | Live-cell imaging (HeLa cells) | 48 |
| | Fluorometric & colorimetric | HEPES buffer (pH 7.0) | 320, 380 | 0.1 μM | 1.19 × 10⁻⁶ | 1 : 1 | — | 49 |
| | Fluorometric | Water | 420, 575 | 0.056 μM | 0.21 × 10⁻² | 2 : 1 | — | 50 |
| | Fluorometric & colorimetric | Tris buffer (10 mM, pH 7.0) | 450, 482 | 1 μM | 1 × 10⁻⁶ | 1 : 1 | Live-cell imaging (HeLa cells) | 51 |
| | Fluorometric & colorimetric | Bis-tris buffer (10 mM, pH 7.0) | 440, 487 | 1.12 μM | 2.1 × 10⁻² | 1 : 1 | Live-cell imaging (human dermal fibroblast) | 52 |
| | Fluorometric & colorimetric | 99% Water/DMSO | 403, 487 | 54 nM | — | 2 : 1 | Aqueous solution and test paper | 53 |
| | Fluorometric & colorimetric | Tris-HCl (10 mM, pH 7.2) | 334, 445 | 336 nM | 4.2 × 10⁻³ | 1 : 1 | — | 54 |
| | Fluorometric & colorimetric | Tris-HCl (0.1 mM, pH 7.2) | 335, 450 | 66.5 nM | 9.5 × 10⁻³ | 2 : 1 | — | 58 |
| | Fluorometric & colorimetric | H₂O/DMSO (50 : 1) | 387, ~490 | 5.1 μM | 7.6 × 10⁻³ | 1 : 1 | — | 59 |
| | Fluorometric & colorimetric | H₂O/DMSO (50 : 1) | 310, ~455 | 3 μM | 2.9 × 10⁻³ | 1 : 1 | — | 59 |
| | Fluorometric & colorimetric | Hexamine buffer (10 mM, pH 5.5) | 380, 536 | 230 nM | 1.84 × 10⁻⁴ | 1 : 1 | — | 66 |
| | Fluorometric & colorimetric | Hexamine buffer (10 mM, pH 5.5) | 315, 475 | 195 nM | 1.30 × 10⁻⁴ | 1 : 1 | — | 67 |
| | Fluorometric & colorimetric | Hexamine buffer (10 mM, pH 5.5) | 315, 475 | 155 nM | 1.76 × 10⁻⁴ | 1 : 1 | — | 67 |
| | Fluorometric | Hexamine buffer (10 mM, pH 5.5) | 315, 475 | (453)⁹ | — | — | — | 67 |
| Polymer-based sensors | Fluorometric | Water | 345, 435 | 9.67 nM | 1.30 × 10⁻³ | 1 : 1 | Real water samples | 70 |
| | Fluorometric | Water | 399, 469 | 6.13 nM | 6.39 × 10⁻³ | 2 : 1 | Real water samples | 68 |
| | Fluorometric | Water | 367, 447 | 4.05 nM | 1.18 × 10⁻³ | 2 : 1 | Live cell (mouse myeloma cells) and real water samples | 71 |
| | Colorimetric | Water | 530/ | 2.0 nM | — | — | Soil samples | 72 |
| | Colorimetric | H₂O/DMF (99 : 1) | 392/ | — | — | — | Live cell (normal lung AT II cells) | 73 |
| Nanomaterial based | Fluorometric | Water | 330, 455 | 14 nM | — | 1 : 1 | Live cell imaging (A549 cells) and real water samples | 74 |
| | Fluorometric & colorimetric | HEPES buffer (pH 7.4, 10 mM) | 363, 511 | 153 nM | 1.99 × 10⁻³ | 1 : 1 | Microfluidic setup for real water samples | 75 |

⁹ Receptor: analyte binding ratio. ⁹ Initial emission wavelength (blue-shifted emission wavelength).
Also, the probe exhibited a remarkable increase in the emission intensity at 470 nm (Fig. 3d), with the lowest detection limit of $6.03 \times 10^{-7}$ M and a strong binding constant of $0.35 \times 10^5$ M$^{-1}$. The bidentate and mono-basic nature of the ligand in the rigid chelated product was supported by $^1$H NMR titration of the probe with Al$^{3+}$ in DMSO-$d_6$ and DFT calculations. Thus, mechanistically, a reduction in the internal charge transfer (ICT) and improved CHEF probably contributes to the selective detection of Al$^{3+}$ via 1 : 1 complexation with 2. The authors also demonstrated the potential capability of the probe for the intracellular imaging of Al$^{3+}$ in HeLa cells.

In the very next year, Singh and coworkers redesigned the probe 2 to construct a biologically interesting product 3 (Scheme 1) where the furan-derivative amine counterpart was replaced by 5-aminouracil to form the imine moiety. The authors claimed that this is the first report on the Schiff-base of 5-aminouracil with NH for the sensing of Al$^{3+}$ through the phenomenon of CHEF. In aqueous media, the keto tautomeric form of the probe selectively chelates with Al$^{3+}$, thus exhibiting an enhancement in the emission intensity at 495 nm (Fig. 4a). Nevertheless, the presence of other cationic species did not alter the fluorescence intensity of the probe. The formation of the stable 1 : 1 complex was established by Job’s plot and electro-spray ionization (ESI) mass analysis. Ligand 3 behaves as a tridentate Schiff-base by coordinating Al$^{3+}$ via the carbonyl of uracil, imine nitrogen, and keto group on the naphthalene ring, as is evident from the $^1$H NMR studies. Further, the binding constant and detection limit were determined to be $(1.5 \pm 0.009) \times 10^3$ M$^{-1}$ and 1.0 $\mu$M, respectively.

Exploiting the similar Schiff-base approach, a novel phenol-naphthol hybrid chemosensor 4 (Scheme 1) was reported by Kim and coworkers in 2014. The developed chemosensor distinguishes Al$^{3+}$ and CN$^{-}$ from other metal ions through fluorescence enhancement and quenching effect in bis–tris buffer and methanolic medium, respectively. A 100-fold increase in the emission intensity at 490 and 515 nm was observed with the gradual addition of 34 equiv. Al$^{3+}$ (Fig. 4b). However, turn-on fluorescence feedback got significantly subdued in the presence of competing metal ions such as Ag$^{+}$, Cu$^{2+}$, Cr$^{3+}$, and Fe$^{3+}$ (Fig. 4c). Mechanistically, 1 : 1 chelation with 4 inhibits the rotation of the aromatic rings around the imine moiety. This brings both the naphthol and phenol rings to the same plane and furnishes a conjugated system that enhances the emission intensity upon Al$^{3+}$ binding. The stability constant of the complex and the lowest detection limit for aluminium ions were found to be $2.5 \times 10^3$ M$^{-1}$ and 0.13 $\mu$M, respectively. In addition, the authors also illustrated the successful tracking of intracellular Al$^{3+}$ in HeLa cells using 4 (Fig. 4d).

Utilizing the excellent sensing properties of HN, in the same year, Liu and coworkers illustrated the design and synthesis of another naphthol aldehyde-tris derivate molecular probe 5 (Scheme 1) for Al$^{3+}$ detection. The UV-Vis absorption spectra revealed a reduction in the O.D. value between 400–420 nm and
310 nm (Fig. 5a) with the concomitant color change of the solution from light yellow to colorless. Concentration-dependent fluorometric titration of aluminium ion (0–2 equiv.) with 5 (10 μM) in HEPES buffer (pH = 7.0) converted the non-fluorescent probe 5 into a blue fluorescent probe. Fig. 5b demonstrates that the developed chemosensor is highly selective to Al\textsuperscript{3+} over other metal ions with a detection limit of 0.1 μM. The large association constant 1.19 × 10\textsuperscript{8} M\textsuperscript{-1} indicated the strong metal–ligand interaction. Further, \textsuperscript{1}H NMR experiments were carried out to investigate the coordinating site of Al\textsuperscript{3+} in the ligand. Interestingly, chemical shifts revealed the ability of three hydroxyl groups of tris to ligate with the aluminium ion forming a 1 : 1 complex. Unlike the previous reports, imine nitrogen and hydroxyl moiety on the naphthalene ring did not participate in forming the Al\textsuperscript{3+} chelated product. The switch-on mechanism of fluorescence emission was attributed to the blockage of the PET mechanism in the 5-Al\textsuperscript{3+} complex.

Inspired from the hard acid–hard base concept in Al\textsuperscript{3+} sensing, in 2017, Yeap and coworkers designed a promising chemosensor 6 that can solely be used in pure water (Fig. 6a).\textsuperscript{50} The probe 6 was incorporated with the –COOH acid moiety, which acts as a hard base and provides good water solubility. Fig. 6b exhibits the UV-Vis spectral changes of 6 with Al\textsuperscript{3+}. The gradual addition of Al\textsuperscript{3+} to the aqueous solution of the probe enhances the emission intensity at 575 nm through the CHEF mechanism (Fig. 6c). Synthesized probe 6 was highly selective to Al\textsuperscript{3+} even in the presence of other metal ions (Fig. 6d). The association constant obtained by the fluorescence titration for the 6-Al\textsuperscript{3+} complex is 0.21 × 10\textsuperscript{2} M\textsuperscript{-1}. Further, Job’s plot analysis and \textsuperscript{1}H NMR titration experiments were performed to understand the binding stoichiometry and mode of interaction (Fig. 6e). It was noticed that the coordination of two oxygen atoms of the carboxylic group, two phenolic oxygen atoms, and two oxygen atoms of the oxymethylene group of the ligand with Al\textsuperscript{3+} resulted in the formation of the 2 : 1 (6 : Al\textsuperscript{3+}) complex (Fig. 6a).

2.2 Julolidine and quinoline-based sensors
The water-soluble julolidine-based imine probes have grabbed immense attention from the scientific community owing to their selective determination of aluminium ions in the
biological system. The imine group attached to julolidine is very fluorescent in the rigid form but C==N isomerization causes quenching due to its flexibility (Fig. 7a). This phenomenon has been exploited by researchers for the selective sensing of aluminium ions. The binding of the probe with the metal provides rigidity to the molecule, which in turn produces a fluorescence response.

J. Y. Noh et al. demonstrated the utilization of a Julolidine-based chemosensor for the selective detection of Al^{3+} in live-cell imaging. They synthesized the chemosensor ortho-
phenyljulolidineimine (7) containing the π-conjugated Schiff base using a julolidine-based imine probe (Fig. 7a). The probe showed an excellent turn-on fluorescence response with a 100-fold increase in the fluorescence intensity upon the addition of $\text{Al}^{3+}$ in an aqueous solution. The 1:1 complexation between 7 and $\text{Al}^{3+}$ was responsible for fluorescence response as it inhibits C==N isomerization and excited-state intramolecular proton transfer (ESIPT) processes. The spectroscopic investigation confirmed the high selectivity and sensitivity for $\text{Al}^{3+}$ and possessed a detection limit of 0.13 μM. They also demonstrated the application in live-cell imaging, where HeLa cells exposed to 0.1 μM $\text{Al}^{3+}$ were discernible from unexposed cells (Fig. 7d).

In 2016, Y. S. Kim et al. further modified the chemosensor and developed 8 by introducing an electron-donating tert-butyl group to enhance the solubility in aqueous solution. However, after introducing the tert-butyl group, the authors measured a slight increase in the LOD value, but it is still less than 7.41 μM, as recommended by World Health Organization (WHO) in drinking water. Receptor 8 alone has weak fluorescence proposed due to ESIPT involving the phenolic proton. This probe showed a 90-fold enhancement of the emission intensity at 487 nm with $\text{Al}^{3+}$ treatment (Fig. 7b). This enhancement was proposed due to the chelation-enhanced fluorescence effect, in which the metal ion induces rigidity after chelation and tends to produce fluorescence. Also, C==N isomerization and ESIPT inhibited after chelation leads to fluorescence enhancement. However, the presence of interfering metal ions such as $\text{Cu}^{2+}$, $\text{Fe}^{2+}$, $\text{Fe}^{3+}$, and $\text{Cr}^{3+}$ causes the quenching of the intensity (Fig. 7c). Probe 8 is a suitable and biocompatible sensor for imaging living cells.

As most of the fluorophores reported do not show high selectivity for only the $\text{Al}^{3+}$ ion, there has always been some interfering metal ion affecting the fluorescence. Achieving high selectivity and specificity for $\text{Al}^{3+}$ ion remains a concern for the scientific community. Quinoline-based fluorophores fascinate scientists to overcome this low selectivity of the $\text{Al}^{3+}$ sensor over the past decade. The ESIPT process in 8-hydroxyquinoline inhibits the fluorescence. Upon binding with the metal ion, the possibility of ESIPT vanishes, which causes turn-on fluorescence. Therefore, researchers well-exploited this phenomenon for aluminium sensing.

In 2017, J. Wang et al. reported hydroxyquinoline-based highly selective $\text{Al}^{3+}$ detection based on a fluorescent chemodosimeter (a system based on analyte-induced irreversible chemical reactions). Compound 9 synthesized by them shows high selectivity with a turn-on fluorescence response to $\text{Al}^{3+}$ in aqueous solution of 99% water/DMSO (v/v) with a fluorescent enhancement of 582-fold (Fig. 8a and b). The ESIPT process due to intramolecular hydrogen bonding between the hydroxy and the nitrogen of quinoline moiety causes fluorescence quenching in 8-hydroxyquinoline derivatives. A after binding with $\text{Al}^{3+}$, the intramolecular hydrogen bond broke and gave rise to an enhancement in the fluorescence (Fig. 8e). On the other hand, two reasons for the high selectivity were proposed. First, the binding abilities of other metal ions are weak and cannot form the complex. Second, the paramagnetic nature of metal ions such as $\text{Cu}^{2+}$, $\text{Ni}^{2+}$, $\text{Co}^{2+}$, and $\text{Fe}^{3+}$ will cause fluorescence quenching after binding with the fluorophore. Fluorophore 9 had excellent sensitivity and could detect down to 54 nmol L$^{-1}$ of $\text{Al}^{3+}$ (Fig. 8e and f). Another advantage of this fluorophore was the rapid detection of $\text{Al}^{3+}$ by the naked eye using a fluorescent test paper (Fig. 8d).
2.3 Coumarin and chromone-based Al\textsuperscript{3+} sensors

Though fluorescent aluminium receptors are reported with various scaffolds, Schiff base sensors hold a strong position because of their flexibility and tunability. Their N and O comprising hard base donor sites provide a favorable coordination sphere for the hard acid Al\textsuperscript{3+}, thereby changing the fluorescent properties of probes upon metal binding.\textsuperscript{54} Schiff base-based receptors mostly follow the photoinduced electron transfer (PET) mechanism, where the electron transfer from the fluorophore to another part of the probe gets inhibited by the coordination of the metal ion, resulting in an increase in the fluorescence signal by the CHEF effect. Among the Schiff bases, oxygen-containing heterocyclic coumarin and chromone-based fluorophores have received considerable attention for the naked-eye detection of trivalent aluminium cations over the past decades.

Coumarin, an extensively studied fluorophore with high fluorescence quantum yield, visible light emission, and large Stokes’ shift stands out as an excellent skeleton for sensing applications.\textsuperscript{55,56} Moreover, comparably less toxicity and ease of modification enable scientists to use coumarin-based aluminium receptors in biological systems. Similarly, chromones are naturally occurring organic molecules with broad pharmacological applications, ranging from anti-inflammatory to anticancer activities. Ideal photophysical and spectroscopic properties of chromones, including strong blue emission, presence of chromophoric C=O and C=C moieties, and small singlet-triplet energy gap have attracted a lot of attention in recent times.\textsuperscript{57}

Though many coumarin and chromone based aluminium sensors have been reported, their limited bioavailability prevents their use in the detection of aluminium in living systems. Recently, researchers are interested in developing probes by wisely grafting water-soluble moieties such as amino acids and polyalcohols to the fluorophores to exploit them \textit{in vivo}.

In 2015, Qi and coworkers developed a coumarin-based fluorescent ‘off–on’ aluminium sensor 10 with great water
solubility attained by attaching an L-histidine moiety.\textsuperscript{34} Probe 10 having an emission maximum of 445 nm showed excellent selectivity and sensitivity toward aluminium cation even in the presence of other biologically relevant metal ions, except Cu\textsuperscript{2+} in physiological conditions (Fig. 9b and c). UV-Vis titration studies, indicating the deprotonation of hydroxyl functionality upon complexation, Job’s plot, and ESI-MS studies, suggested a 1 : 1 stoichiometry between the quadridentate ligand and Al\textsuperscript{3+}. With the aid of \textsuperscript{1}H NMR, authors reasonably propose a sensing mechanism based on the PET phenomenon, where the electron transfer from the Schiff base nitrogen gets inhibited upon metal binding as the lone pairs are no longer available, leading to an increased fluorescence signal (Fig. 9a). Apart from enhancing the bioavailability, the acid group of L-histidine acts as a hard base donor site for metal coordination. Interestingly, 10 also has a greater sensitivity toward Cu\textsuperscript{2+} but no fluorescence emission since the complexation does not involve the Schiff base nitrogen and thereby the PET process and the CHEF effect.

Following the line, the same group developed yet another aluminium sensor 11 based on the coumarin-L-serine hybrid moiety.\textsuperscript{58} The amine part of the Schiff base was sensibly chosen to enhance the water solubility and to provide coordination sites. As Fig. 10b and c suggests, the highly quantum efficient probe exhibited great selectivity toward Al\textsuperscript{3+} and Zn\textsuperscript{2+}. However,
the interference of other metal ions quenched the fluorescence significantly for the latter in aqueous media (Fig. 10d). The blue emitting ‘turn-on’ sensor binds with aluminium having a 2 : 1 stoichiometry following the well-explored PET process. Electron transfer from the Schiff base nitrogen and oxygen of L-serine gets repressed upon the coordination of Al$^{3+}$, relapsing the CHEF signal (Fig. 10a).

In 2016, Vladimir Král and coworkers synthesized two novel water-soluble blue-emitting chromone based-Schiff bases having high affinity toward Al$^{3+}$ (Fig. 11).

The grafting of the polyhydroxylated glucitol moiety improved the bioavailability to a greater extent. The computational studies suggested that 12 can bind to Al$^{3+}$ in 1 : 1 ratio, whereas 13 can bind either as 1 : 1 or 2 : 1, the latter being one of the strongest coordination having log($K$) = 9.32.

Though several coumarin and chromone-based water-soluble aluminium sensors with desirable association constants and detection limits have been developed, their potential bioanalytical applications are seldom investigated.

### 2.4 Peptide and polymer-based Al$^{3+}$ sensors

Besides single amino acids, the combination of conjugated fluorophores with short peptides opens up a new arena of ion-selective probes with immense scope in biological systems. The high water-solubility, biocompatibility, structural diversity, and excellent metal ion binding ability of peptides make them a potential candidate for sensing applications.

Since hard Al$^{3+}$ binds easily with negatively charged oxygen donor groups, amino acids such as Glu, Ser, Asp, or Thr are preferred in peptide-based aluminium receptors. On the other hand, the immobilization of conventional small molecular probes onto hydrophilic polymer matrix is also an emerging strategy to develop biocompatible sensors. Similar to peptides, polymers possess desirable characteristic features such as better water solubility, simplicity of use, signal amplification, and ease of fabrication into devices. Peptide and polymer-based sensors show exceptional bioavailability and ultrasensitive detection regardless of their bulky structures.

Lee and coworkers reported the first-ever peptide-based water-soluble reversible aluminium sensor 14 in 2016 by grafting a tripeptide (Ser–Glu–Glu) with dansyl fluorophore bearing a sulfonamide group, which can act as a ligand for hard metal ions (Fig. 12a).

Emission studies revealed that the ‘turn-on’ probe has excellent sensitivity toward Al$^{3+}$ in acidic aqueous buffered solution with a detection limit in the nanomolar range. The sensing was associated with an eight-fold emission enhancement and a 20 nm blue shift (536 nm to 516 nm), resulting in a color change from yellow to bright green under UV light (Fig. 12b and c). However, the detection ability was pH dependent within the range of 4–7 and a maximum at pH = 5.5. Job’s plot and ESI-MS confirm the 1 : 1 stoichiometry along with
the indication of carboxyl group deprotonation upon complexation. The downfield shifts of protons of α-carbons in 1H NMR suggests a quadra-coordinating binding mode where the hydroxyl and carboxyl group of tripeptide and sulfonamide group of dansyl moiety contribute in Al3+ chelation.

Following the same line, Ramezanpour and coworkers improved the detection ability by replacing the dansyl probe with more water-soluble and cheaper 2-aminobenzoyl moiety, keeping the tripeptide the same to give 15.67 The authors designed another chemosensor 16 with the same fluorophore

![Image](https://example.com/image1.png)

**Fig. 10** (a) The plausible binding mode of 11 with Al3+ and fluorescence mechanism of the PET processes. (b) Fluorescence spectra (10.0 μM, λex = 335 nm) with the addition of various metal ions (10.0 equiv.) in aqueous solution (Tris–HCl, 10 mM, pH 7.2). (c) Fluorescence spectra (10.0 μM, λex = 335 nm) upon the titration of Al3+ (0–2.5 equiv.) in aqueous solution (Tris–HCl, 10.0 mM, pH 7.2). (d) Fluorescence responses (10.0 μM, λex = 335 nm) to various metal ions (10.0 μM) (black column) (10 equiv.) and upon the subsequent addition of Al3+ (red column) in aqueous solution (Tris–HCl, 10 mM, pH 7.2). Reprinted with permission from ref. 58 copyright 2015. Japan Society for Analytical Chemistry.

![Image](https://example.com/image2.png)

**Fig. 11** Fluorescence response of compounds 12 and 13 on addition of the selected cations. Reprinted with permission from ref. 59 copyright 2017. Taylor & Francis Academic Journals.
based on the heptapeptide sequence Ala–Glu–Pro–Glu–Ala–Glu–Pro, a naturally occurring Apidaecin 1 gene peptide with three glutamic acids, which can potentially act as ligating sites for Al$^{3+}$. Both turn-on fluorescent sensors are highly specific and selective to Al$^{3+}$ in water with emission maxima at 475 nm after complexation (Fig. 13c and d). Similar to 14, these sensors are also sensitive to pH, working efficiently between pH 4–7, and the 1 : 1 ion binding brings a prominent blue shift of 20–23 nm (Fig. 13e and f). A deeper investigation with the aid of spectroscopic techniques deciphered the ‘off–on’ mechanism based on ICT. 2-Aminobenzoyl moiety act as the electron donor, whereas the amide group of the first amino acid attached to the donor, acts as the electron-withdrawing moiety and binds to the guest cation, lowering the HOMO–LUMO energy gap and facilitating ICT, thereby giving fluorescence enhancement (Fig. 13a and b).

In 2019, Wang and coworkers reported three polymer-based highly selective and sensitive ‘turn-on’ Al$^{3+}$ sensors by incorporating conventional Schiff base fluorophores onto the non-toxic, biocompatible, water-soluble polyethylene glycol (PEG) matrix. The one-step esterification of benzoylhydrazine Schiff base derivative with carboxylated PEG yielded 17 with a 1 : 1 stoichiometry and an excited state intramolecular proton transfer (ESIPT)-based sensing mechanism upon complexation. The chelation of Al$^{3+}$ stops the C=N isomerization and restricts the ESIPT process, making the complex rigid and thereby enhancing fluorescent intensity to a greater extent (Fig. 14a).

While the grafting of PEG with naphthol- and salicylidene-based Schiff bases resulted in 18 and 19, respectively, which binds with Al$^{3+}$, having a 2 : 1 ratio. Both sensors were non-fluorescent in their free state due to the photoinduced electron transfer (PET) from imine to naphthalene or benzene rings, but the rigidity arising from complexation prevents the process, resulting in a bright blue/cyan emission (Fig. 14b and c). All three sensors could detect Al$^{3+}$ even in the presence of other highly concentrated analytes, with a quick response time below 20 seconds over a wide range of pH from 5 to 10 (Fig. 14d–i). The reversible recognition property makes them monomolecular circuits, exhibiting an INHIBIT type logic gate with Al$^{3+}$ and EDTA (displaces Al$^{3+}$, thereby halting the fluorescence) as the two chemical inputs and the emission intensity at the maxima as the output (Fig. 14k). Sensors 17 and 19 could also give promising results in the naked-eye detection of Al$^{3+}$ in real water samples using test strips (Fig. 14j and l).

### 2.5 Nanomaterials-based Al$^{3+}$ sensors

Nanomaterials-based sensing platforms are gaining immense attention. In this direction, plasmonic, semiconductor-based, and carbonaceous nanoparticles are mostly getting preference compared to other metal oxide nanoparticles. Generally, the plasmonic band of the novel metals displays a visible color due to the interaction of free electrons on metals and electromagnetic fields. Most importantly, the optical absorption property of plasmonic particles is sensitive to the local dielectric of the surrounding medium. Such environment-sensitive plasmonic properties of the most frequently utilized copper, silver, and gold nanoparticles have shown a great promise for sensing...
bioanalytes, metal ions, and environmentally important small molecules. On the other hand, semiconductor-based luminescent nanoparticles, popularly known as quantum dots, are also employed for sensing applications. In the latter case, the turn-on-off or ratiometric responses are utilized for designing the sensing platform.

In 2013, Wu and coworkers have developed a sensing method for Al$^{3+}$ in water at pH 7.4 utilizing silver nanoparticles.
The synthesized Ag-NPs were suitably decorated with an Al\textsuperscript{3+} binding ligand, namely, 8-hydroxyquinoline-5-sulfonate. Upon the addition of Al\textsuperscript{3+} ions, these modified Ag-NPs show a distinct color change from yellow to deep orange as well as a strong enhancement in the fluorescence emission. The absorption and emission-based titrations showed high nanomolar sensitivity and good selectivity toward Al\textsuperscript{3+} ions over other metal ions. Further, the authors determined Al\textsuperscript{3+} ions in living mouse myeloma cells via fluorescence imaging.

Fig. 14 Structures and proposed binding modes of 17 (a), 18 (b), and 19 (c). Fluorescence spectra of 10 \(\mu\text{M}\) 17 (d), 18 (e), and 19 (f) in the presence of various metal ions (2 equiv.) in aqueous solution. Inset: The photograph of 17, 18, and 19 with various metal ions (2 equiv.) in aqueous solution under a 365 nm UV lamp. Competition analysis of 10 \(\mu\text{M}\) 17 (g), 18 (h), and 19 (i) to various metal ions in aqueous solutions. The black bars represent the intensity when mixed with 2 equiv. of other metal ions; the red bars represent the intensity when mixed with 2 equiv. of Al\textsuperscript{3+} and 2 equiv. of other metal ions. (j) Fluorescent detection of Al\textsuperscript{3+} using 17 by test paper under a 365 nm UV lamp after being immersed in different aqueous solutions (10\textsuperscript{-4} M) (from left to right, up: blank, Al\textsuperscript{3+}, Co\textsuperscript{2+}, Cr\textsuperscript{3+}, Cu\textsuperscript{2+}, and Fe\textsuperscript{3+}; down: Hg\textsuperscript{2+}, Mn\textsuperscript{2+}, Na\textsuperscript{+}, Ni\textsuperscript{2+}, Pb\textsuperscript{2+}, and Zn\textsuperscript{2+}). (k) The monomolecular circuit for the INHIBIT logic gate. (l) Photographs of 19 test strips under a 365 nm UV lamp after being dipped into aqueous solutions of different metal ions (100 \(\mu\text{M}\)) (from left to right, up: Ba\textsuperscript{2+}, Ce\textsuperscript{3+}, Cd\textsuperscript{2+}, Co\textsuperscript{2+}, Al\textsuperscript{3+}, Cr\textsuperscript{3+}, Cu\textsuperscript{2+}, and Fe\textsuperscript{3+}; down: Hg\textsuperscript{2+}, In\textsuperscript{3+}, K\textsuperscript{+}, Mn\textsuperscript{2+}, Na\textsuperscript{+}, Ni\textsuperscript{2+}, Pb\textsuperscript{2+}, and Zn\textsuperscript{2+}). Reprinted with permission from ref. 68 and 70 copyright 2019. Elsevier.
The mechanism of colorimetric and fluorometric detection is associated with the aggregation of Ag-NPs (as shown in Fig. 15a–d) mediated by the 8-hydroxyquinoline-5-sulfonate ligand, a selective binder for Al\(^{3+}\). The authors have observed a ratiometric response in the optical absorption upon the addition of different concentrations of Al\(^{3+}\) ions. Such changes in the

![Image](https://example.com/image.png)
optical absorption result in a visible color change of the solution. The plasmonic band at 392 nm shifted toward red and a new peak at 530 nm appeared due to the Al$^{3+}$-induced aggregation of Ag-NPs. Upon the addition of Al$^{3+}$, the emission intensity got enhanced by 3 times due to the inhibition of photoinduced electron transfer from the involvement of lone-pair of electrons from the quinolone nitrogen atom due to Al$^{3+}$ binding.

Later, in 2014, Kaur and colleagues developed 1,8-naphthalimide-based organic nanoparticles (ONPs, 21) for the sensing of Al$^{3+}$ in aqueous media, as shown in Fig. 16a.$^{22}$ The molecule itself has an emission maximum at 390 nm in DMF. However, after the formation of ONPs, due to the J-type nano-aggregation, a new peak at 494 nm was observed along the existing peak at 394 nm (Fig. 16b). The morphology and size of ONPs were assessed using TEM and dynamic light scattering.
experiments, respectively. A representative TEM image is shown in Fig. 16c. The developed sensor is highly selective toward Al$^{3+}$ and sensitive with a detection limit of 0.67 μM. A significant enhancement of both the emission band was observed upon the addition of only Al$^{3+}$ and metal ions have a negligible effect on the emission property (as shown in Fig. 16d and e). The intensity-based kinetic measurement shows a very fast response time of the sensor and within 120 seconds, a saturation of the emission signal was obtained (Fig. 16f). The sensor system was further utilized to determine the Al$^{3+}$ content of river water and acidic soil. The fluorescence enhancement of ONPs with the addition of Al$^{3+}$ was due to the reduction of photoinduced electron transfer (PET) from the central nitrogen of the diethylenetriamine linker part to electron-deficient Al$^{3+}$. The sensing mechanism was validated using DFT calculation.

Recently, Wang and coworkers presented a fluorescence-based Al$^{3+}$ sensing method using thiolated fluorescence gold nanocluster (Au NCs, 22). The synthetic method was an easy, green, and one-pot synthesis in an aqueous solution. The synthesized GHS-Au NCs were highly stable, ultrasmall, and monodisperse in size with a diameter of 1.4 nm. The large Stokes-shifted emission of GSH-Au NCs shows a fluorogenic response with >40-fold enhancement upon binding with Al$^{3+}$ (as shown schematically in Fig. 17a). The designed probe has shown a great selectivity for Al$^{3+}$ ions and the digital photo at the inset of Fig. 17b also demonstrates the selectivity of Al$^{3+}$ ions over other ions in an aqueous solution. The fluorescence intensity of GSH-Au NCs also displays a linear increase in the fluorescence intensity with increasing concentration of Al$^{3+}$ from 0–600 μM (Fig. 17c). Furthermore, the authors demonstrated the suitability of the probe for imaging a high concentration of Al$^{3+}$ in live cells, as shown in Fig. 17d and e.

Fig. 18  AIE-based sensing of Al$^{3+}$. (a) Schematically showing the AIE process and Al$^{3+}$ sensing. Cuvette picture show fluorescence color change upon AIE and Al$^{3+}$ binding. (b) Effect of water addition in DMF solution of the probe causes emission enhancement due to AIE. (c) effect of metal ions on the emission property to show the selectivity toward Al$^{3+}$ ions. (d–f) Fluorescence images of A549 cells (d) brightfield, in the presence (f), and absence of Al$^{3+}$ (e). Reprinted with permission from ref. 74 copyright 2019. Wiley-VCH.
2.6 Water-soluble aggregation induced emission (AIE)-based Al\(^{3+}\) sensors

AIE-based sensing platforms are becoming popular due to their synthetic variation, suitable tunability, and high sensitivity. Recently, in 2019, Li and coworkers have reported a Schiff’s base derivative (23), which shows a marked AIE response and specific Al\(^{3+}\) ion binding property. The weakly-fluorescent Schiff’s base compound in DMF turns into a strong green-emissive solution with an emission maximum of about 510 nm upon the addition of more than 40% water (schematically, the AIE process and Al\(^{3+}\) sensing are demonstrated in Fig. 18a and b). The weak fluorescence emission of probe 23 is due to the fast rotation of the furyl group and C=N isomerization. Upon aggregation, these paths of non-radiative de-activation get restricted and cause a turn-on AIE response. Further, upon the addition of Al\(^{3+}\) ions in this green-emission solution, the fluorescence emission showed a significant blue shift from 520 nm to 455 nm (as shown in Fig. 18c). The blue-shifted and enhanced emission of the 1:1 complexation of probe 23 and Al\(^{3+}\) is due to restricted intramolecular movements. Other metal ions did not cause any change in the fluorescence emission. This result indicated an excellent specificity for Al\(^{3+}\) ions over other metal ions. The developed method has very fast response time (within few minutes) and a suitable pH window for Al\(^{3+}\) detection. As an application of this method, the authors performed live-cell laser confocal microscopy using A549 lung cancer cells. Cells treated with Al\(^{3+}\) showed a strong enhancement in the fluorescence emission coming from the cells compared to the same without Al\(^{3+}\), indicating good cellular permeability and confirming excellent fluorescence imaging capabilities.

Leray and coworkers in 2019 reported 4-propoxysulfonate salicylaldehyde azine (PSSA, 24)-based water-soluble fluorescent sensor based on the AIE enhancement (AIEE) effect. The structure of PSSA is provided in Fig. 19a. PSSA is highly soluble due to the presence of negatively charged sulfonate groups. However, with increasing concentration of ethanol content, there is a dramatic enhancement of the emission intensity, as shown in Fig. 19b. Upon the addition of Al\(^{3+}\) ions in PSSA solution, there is a significant 100-fold enhancement in the emission intensity due to the complexation-assisted aggregation of PSSA, as schematically shown in Fig. 19c and d. PSSA has also shown good specificity over other metal ions (Fig. 19e) with rapid response time.

3. Conclusions

The springing number of optical probes holds promise to overcome the challenges for the effective, convenient, and rapid detection of Al\(^{3+}\) sensing. Water solubility is the desideratum for efficient fluorescent probes in biological applications. The preceding sections illustrated the different classes of water-

![Fig. 19](image_url)
soluble fluorescent sensors to detect Al³⁺ in real-time biological application. The strategies used based on PET, ES IPT, C=N isomerization, and CHEF effect are deciphered for the development of turn-on fluorescent probes. This review summarized the findings of several probe’s photophysical properties, detection limit, selectivity, and detection mechanism.

Water being the most common medium for the mobilization of aluminium to the biosphere is strictly regulated and quality controlled by health organizations. The Environmental Protection Agency (EPA) and WHO recommend a Secondary Maximum Contaminant Level (SMCL) of 0.05–0.2 µg mL⁻¹ and 0.2 µg mL⁻¹, respectively, for aluminium in drinking water.⁷⁶ The optical sensors discussed in this review can detect Al³⁺ much lower than the SMCL. However, many of them are not utilized for practical applications, and their biocompatibility remains a question to employ in biological systems. Although various probes with certain modifications have been developed, there is still a requirement for highly photostable, selective, and sensitive probes with good aqueous solubility to avoid the usage of mixed aqueous-organic solvent systems. To date, the detection of Al³⁺ was achieved in real water samples and live-cell imaging, but clinical utility requires deep tissue and in vivo imaging. In this regard, there is significant scope for developing red-emitting fluorescent probes to provide deep tissue penetration depth with negligible autofluorescence. Moreover, interference from other metal ions restricted the exploitation of optical sensors for potential applications in complex biological systems. Future research toward the innovation of highly selective, sensitive, and water-soluble fluorescent probes opens the door for practical applications. The authors believe that this review furnishes in-depth mechanistic information to readers who are fascinated by the emerging field of Al³⁺ sensors for biological application.

Conflicts of interest

There is no conflict of interest to declare.

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References

1 E. Monosson, in *Evolution in a Toxic World: How Life Responds to Chemical Threats*, Island Press/Center for Resource Economics, Washington, DC, 2012, pp. 48–64, DOI: 10.5822/978-1-61091-221-1_4.
2 C. D. Foy, R. L. Chaney and M. C. White, *Annu. Rev. Plant Physiol.*, 1978, 29, 511–566.
3 M. Schmitt, T. Watanabe and S. Jansen, *AoB Plants*, 2016, 8, plw065.
4 R. A. Yokel, *Neurotoxicology*, 2000, 21, 813–828.
5 C. Poschenrieder, B. Gunse, I. Corrales and J. Barcelo, *Sci. Total Environ.*, 2008, 400, 356–368.
6 E. Bojorquez-Quintal, C. Escalante-Magana, I. Echevarria-Machado and M. Martinez-Estevez, *Front. Plant Sci.*, 2017, 8, 1767.
7 F. P. Veitch, *J. Am. Chem. Soc.*, 2002, 26, 637–662.
8 M. A. Qifu, Z. Rengel and J. Kuo, *Ann. Bot.*, 2002, 89, 241–244.
9 L. V. Kochian, M. A. Pineros and O. A. Hoekenga, *Plant Soil*, 2005, 274, 175–195.
10 E. Delhaize and P. R. Ryan, *Plant Physiol.*, 1995, 107, 315–321.
11 D. L. Jones, E. B. Blancaflor, L. V. Kochian and S. Gilroy, *Plant Cell Environ.*, 2006, 29, 1309–1318.
12 X. B. Zhang, P. Liu, Y. Yang and G. D. Xu, *Bot. Stud.*, 2007, 48, 435–444.
13 X. J. Zhao, E. Sucoff and E. J. Stadelmann, *Plant Physiol.*, 1987, 83, 159–162.
14 S. Ishikawa and T. Wagatsuma, *Plant Cell Physiol.*, 1998, 39, 516–525.
15 J. W. Huang, D. L. Grunes and L. V. Kochian, *Plant Soil*, 1995, 171, 131–135.
16 E. Olivares, E. Pena, E. Marcano, J. Mostacero, G. Aguilar, M. Benitez and E. Rengifo, *Environ. Exp. Bot.*, 2009, 65, 132–141.
17 I. O. Igwenagu and N. A. Igwenagu, *Interdiscip. Toxicol.*, 2019, 12, 45–70.
18 C. Exley and E. Clarkson, *Sci. Rep.*, 2020, 10, 7770.
19 K. E. Page, K. N. White, C. R. McCrohan, D. W. Killilea and G. J. Lithgow, *Metallomics*, 2012, 4, 512–522.
20 J. Kamalov, D. O. Carpenter and I. Birman, *J. Toxicol.*, 2011, 2011, 796719.
21 S. Biswas, V. Sharma, P. Kumar and A. L. Koner, *Sens. Actuator B-Chem.*, 2018, 260, 460–464.
22 R. Roy, R. Bhowal, V. Sharma, D. Chopra and A. L. Koner, *J. Mater. Chem. C*, 2021, 9, 1778–1785.
23 R. Roy, N. R. Sajeev, V. Sharma and A. L. Koner, *ACS Appl. Mater. Interfaces*, 2019, 11, 47207–47217.
24 P. Kumar, S. Biswas and A. L. Koner, *New J. Chem.*, 2020, 44, 10771–10775.
25 S. Mallick, F. Chandra and A. L. Koner, *Analyst*, 2016, 141, 827–831.
26 A. Silswal, A. Kanojiya and A. L. Koner, *Front. Chem.*, 2022, 10, 840297.
27 D. Das, R. Alam, A. Katarkar and M. Ali, *Photochem. Photobiol. Sci.*, 2019, 18, 242–252.
28 S. Goswami, S. Paul and A. Manna, *RSC Adv.*, 2013, 3, 10639–10643.
29 B. Liu, P. F. Wang, J. Chai, X. Q. Hu, T. Gao, J. B. Chao, T. G. Chen and B. S. Yang, *Photochem. Photobiol. Acta A Mol. Biomol. Spectrosc.*, 2016, 168, 98–103.
30 A. Barba-Bon, A. M. Costero, S. Gil, M. Parra, J. Soto, R. Martinez-Manez and F. Sancenon, *Chem. Commun.*, 2012, 48, 3000–3002.
31 S. Goswami, K. Aich, S. Das, A. K. Das, D. Sarkar, S. Panja, T. K. Mondal and S. Mukhopadhyay, *Chem. Commun.*, 2013, 49, 10739–10741.
