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Optical detection strategies for Ni(II) ion using metal–organic chemosensors: from molecular design to environmental applications

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Nickel is an important element utilized in various industrial/metallurgical processes, such as surgical and dental prostheses, Ni–Cd batteries, paint pigments, electroplating, ceramics, computer magnetic tapes, catalysis, and alloy manufacturing. However, its extensive use and associated waste production have led to increased nickel pollution in soils and water bodies, which adversely affects human health, animals and plants. This issue has prompted researchers to develop various optical probes, hereafter luminescent/colorimetric sensors, for the facile, sensitive and selective detection of nickel, particularly in biological and environmental contexts. In recent years, numerous functionalized chemosensors have been reported for imaging Ni²⁺, both *in vivo* and *in vitro*. In this context, metal-based receptors offer clear advantages over conventional organic sensors (*viz.*, organic ligands, polymers, and membranes) in terms of cost, durability, stability, water solubility, recyclability, chemical flexibility and scope. This review highlights recent advancements in the design and fabrication of hybrid receptors (*i.e.*, metal complexes and MOFs) for the specific detection of Ni²⁺ ions in complex environmental and biological mixtures.

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1. Introduction

Group 10 metals such as nickel (Ni), palladium (Pd) and platinum (Pt) are widely used in various critical aspects of human life, including industries, material science, medicine and biology.^{1–8} They are typically employed in the manufacturing of various electrical components, alloys and pharmaceuticals, among others.^{1,9–15} Due to the distinct reactivity of the ionic forms of these metals, a significant range of related (bio)active molecules has been designed and developed.¹⁶ However, mis-handling and/or overuse of these metals has caused serious contamination in our ecological systems, particularly in soil and water systems, with significant environmental and biomedical consequences.^{4,17–24}

Among the group 10 metals, nickel is essential for human life due to its involvement in various metabolic processes.^{6,25,26} However, both nickel deficiency and excess intake are associated with numerous health effects. For instance, a concentration exceeding 0.07 mg L⁻¹ of nickel in the body can lead to lung fibrosis, dermatitis, asthma, cancer,

and other allergic reactions.^{17,27} Furthermore, nickel compounds have been classified as ‘category 1 carcinogens’ to humans by the International Agency for Research on Cancer (IARC) since 1990.²⁸ Consequently, the World Health Organisation (WHO) has established a concentration limit of 0.02 mg L⁻¹ for Ni-based ions in drinking water.²⁹ Hence, there is an urgent demand to develop rapid, effective, and reliable methods for detecting Ni(II) ions, particularly in environmental and biological samples.

In contrast to conventional techniques,^{30–35} optical (luminescent or colorimetric) detection methods have gained considerable attention from researchers due to their advantages of rapid (less than 10 min or instantaneous), sensitive (*i.e.*, ppb level), non-destructive facile recognition of various metal ions and other biologically or environmentally important analytes.^{18,36,37} Conceptually, an optical sensor consists of three key components: (i) a binding unit or receptor to display specific binding with the target analyte; (ii) a photoactive unit to emit a signal in the form of luminescence or chromogenic response upon analyte–receptor interaction and (iii) a spacer group or linker to regulate the electron/energy transfer between the receptor and the photoactive unit.³⁸ Optical sensors may be commonly classified into two categories depending on the signal emitted from their photoactive unit or signaling unit, as follows: (i) luminescent sensors, with the

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ability to display distinct luminescence responses in the presence or absence of an analyte,³⁹ which is significant for dynamic monitoring, and (ii) the colorimetric sensors, which allow the naked-eye detection of guest analytes based on color changes. To some extent, colorimetric sensors may be comparatively deemed more promising due to their simplicity, on-site and real-time analysis, and relatively lower capital cost.⁴⁰

Thus, over the past few years, a broad range of luminescent and colorimetric probes based on small organic^{41–45} and inorganic molecules,^{46–48} metal–organic frameworks (MOFs)^{49–51} and nanomaterials^{52–55} has been specifically developed for the recognition of Ni(II) ions. Distinctive from the typical organic sensors, metal-based probes tend to exhibit improved cation sensing and selectivity properties. Additionally, metal-based receptors and their implicit highly flexible chemistry and design (structure, nature, *etc.*) show some compelling features including notably rich and fine tuning of their optical properties (*e.g.*, absorption/emission in the visible region), redox and photostability, magnetism, catalysis, and improved solubility in aqueous medium.^{56–60} Also, the integration of these features into sensor technology is indirectly paving the way for multifunctional platforms with diverse viable applications. Therefore, this work aims to summarize the state-of-the-art in the development of both luminescent and colorimetric probes, specifically metal–organic probes for the detection of Ni²⁺ ions, highlighting their recent developmental progress. Contextually, to the best of our knowledge, the optical detection of Ni²⁺ by various types of metal-based receptors (*e.g.*, metal complexes and MOFs) has not been extensively reviewed to date. Indeed, several reviews have been recently reported on the fluorometric and colorimetric detection of Ni²⁺ ions;^{61–63} however, they were dedicated to organic fluorophores or restricted to one specific type of probe such as ratiometric and near-infrared (NIR) based probes. Hence, an updated inventory of the receptors reported in the last 25 years for the specific detection of Ni²⁺ has been assessed and systematically ordered by the incremental intricacies of the probes ranging from metal complexes to MOFs. Finally, the existing probe design opportunities, challenges and promising development prospects are presented.

2. Probe design: luminescent vs. colorimetric probes

Integrating an organic or inorganic (*e.g.*, metal complex)-based chromophore with a specific receptor is the prototypical approach to design a cation-responsive luminescent or colorimetric probe. In these probes, the binding of metal ions to the receptor consistently alters its luminescence, absorbance and/or relaxivity,^{38,64} confirming the presence of the guest analyte (*i.e.*, metal ion). For these receptors to be functional, either intermolecular or intramolecular interactions between the signaling unit and the receptor unit are required, with an implicit distinction between luminescent and colorimetric probes.^{40,64} Indeed, luminescent sensors are typically related to various

photoinduced electron/energy transfer processes. Several mechanisms, notably PeT (photoinduced electron transfer),^{65–67} PCT (photoinduced charge transfer)^{68,69} and FRET (fluorescence resonance energy transfer),^{70,71} have been explored and frequently adopted to design luminescent molecular probes. Alternatively, several other mechanisms, *e.g.*, metal-bound inhibited ESIPT (excited-state intramolecular proton transfer)^{72,73} and AIE (aggregation-induced emission),^{74–76} have also been established for the design of these probes. Among these mechanisms, PeT is considered the typical mechanism for most of the reported cation-responsive luminescent probes, while the intramolecular charge transfer (*i.e.*, ICT) process is commonly observed for colorimetric probes, and thus the only PeT and ICT mechanisms are further detailed hereafter.

2.1 PeT process in luminescent probes

A typical PeT probe consists of three important components, *i.e.*, a signaling unit (*i.e.*, luminophore), a spacer unit (*i.e.*, linker) and a receptor (*i.e.*, ionophore or binding unit) (Fig. 1).^{38,77} Usually, the ionophore is an electron (e^-) donor such as thio- or amino- containing groups, whereas the luminophore acts as an e^- acceptor. In the case of the free probe (without guest analyte) (Fig. 1(a)), an e^- present in the HOMO (highest-occupied-molecular-orbital) of its luminophore is promoted to the LUMO (lowest-unoccupied-molecular-orbital) with the absorption of a photon of suitable wavelength (excited luminophore). If the energy level of the HOMO of the free ionophore is slightly higher than the HOMO of the luminophore, spatial electron transfer will take place from the ionophore to the luminophore through HOMOs (Fig. 1(a)). Consequently, the transition of the excited electron from the LUMO to HOMO of the luminophore is blocked; this quenching of emission is defined as the PeT process.^{78,79} Metal ion binding to the ionophore results in a decrease in the HOMO energy of the ionophore below the HOMO level of the luminophore, ultimately restoring the luminescence response of the probe (Fig. 1(b)). This phenomenon of luminescence recovery

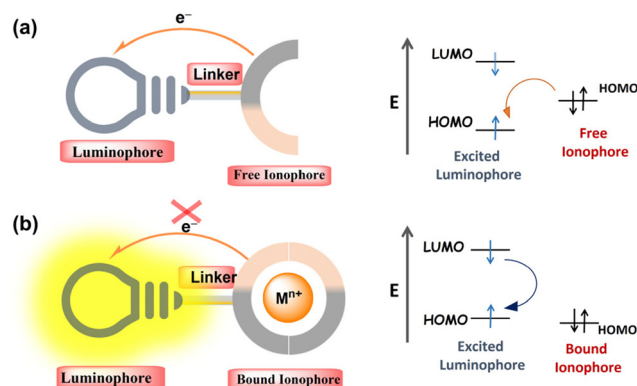


Fig. 1 Schematic “turn-on” sensing mechanism in PeT luminescent probes for metal ion targets; (a) free probe and (b) probe with target metal ion.

is also known as the metal-chelation-enhanced-luminescence effect.^{77–79} The restoration of the luminescence and the emission of the resultant metal complex is often attributed to the $\pi \rightarrow \pi^*$ excited-state relaxation of the luminescence. Notably, the protonation of the ionophore group may also block the PeT event.⁸⁰

Over the past 30 years, numerous cation-responsive luminescent PeT probes have been documented in the literature. However, PeT-based probes may still display shortcomings, and thus there are still developmental obstacles that need to be addressed. For instance, although near-infrared (NIR)-active probes are gaining increasing attention from researchers due to their deep tissue-penetration ability and relatively low phototoxicity, they suffer from low analyte-induced-emission-enhancement factor and large background luminescence.^{81,82} Indeed, in the case of NIR probes, generally a higher HOMO energy level of the luminophore reduces the energy gap between the HOMOs of the luminophore and ionophore. As a result, the PeT process becomes less efficient to quench the emission of the free probe. Hence, the development of ‘turn-on’-responsive NIR probes with the PeT mechanism and low background is still a challenging but pertinent task.⁸³ Moreover, the alternative two-photon (TP) excitable PeT probes may be emphasized to achieve practical bio-imaging applications.⁸⁴

2.2 ICT process in colorimetric probes

Distinct from luminescent receptors, colorimetric sensors are associated with changes observed in their electronic properties in the form of inter- or intramolecular charge transfer (ICT), *e.g.*, ligand-to-metal-charge-transfer (LMCT) and metal-to-ligand-charge-transfer (MLCT) transitions (Fig. 2).⁸⁵ A molecular sensor with the D– π –A system is commonly used to accomplish the colorimetric sensing of metal ions. Further, the D– π –A molecular system can be obtained by introducing both electron donor (D) and electron acceptor (A) groups in the molecular sensor at suitable positions. Metal ion binding to either D or A in the molecular probe occurs

via the hard and soft acid and base (HSAB) principle.⁸⁶ In general, the metal ion binding to D reduces its electron-donating ability, ultimately converting the D– π –A molecular system to A– π –A; as a result, the conjugation of the system is reduced, leading to a blue-shift in the absorption spectrum of the probe (due to the occurrence of an LMCT transition) (Fig. 2(a)).^{85,87} Comparatively, metal ion binding to the A moiety endows the D– π –A system with remarkable strength, leading to an increase in the push–pull intramolecular charge transfer effect with a concomitant red-shift in its UV-Vis spectrum (due to the occurrence of an MLCT transition) (Fig. 2(b)).^{85,88} These types of cation-induced transitions together with ICT contribute to the color changes observed after binding with the target.

A systematic evaluation of various sensors prompted us to discern the optical behaviors of different metal-based sensors towards the target analytes. It was noticed that in most cases, metal complexes and MOFs rely on the PeT mechanism for the luminescent detection of metal ions. This review mainly focuses on the recent progress and limitations to date in the development of Ni²⁺-responsive probes. Thereafter, the luminescent and colorimetric metal-based receptors for Ni²⁺ ions are assessed and described with their photophysical behaviors. The selected probes are carefully classified based on their progressive intricacies as the first criterion, ranging from metal complexes to MOFs. Besides, perspectives are presented in an attempt to further rationalize the development and optimization processes of these luminescent and colorimetric metal-based receptors.

2.3 Fundamental aspects for Ni²⁺ selectivity

The design of the binding motif (or receptor) in a cation-responsive probe is a crucial parameter to achieve selectivity for a specific metal ion (*i.e.*, target analyte) over other competing species. To improve the receptor-cation interaction and the metal ion selectivity, the following aspects must be notably considered:

(i) *Size of the receptor pocket*: the effective ionic radius of the Ni²⁺ ion may vary between 49.0 pm and 69.0 pm depending on the number and nature of the coordinating ligands.⁸⁹ Hence, a selective probe for Ni²⁺ ions can be achieved by fine tuning the receptor pocket within this range; concurrently, it should exclude the risk of the probe response/affinity towards larger or shorter cations or other competing species.

(ii) *The nature and number of donor atoms in the receptor unit* and (iii) *the geometry of the receptor pocket*: Ni²⁺ is a first-row transition metal ion with a d⁸ electronic configuration. It has a tendency to form tetrahedral, square planar, and octahedral complexes. Notably, the square planar geometry is dominant over the tetrahedral geometry, and thus a receptor pocket bearing strong-field ligands and four donor sites must be incorporated in the Ni²⁺ core. Therefore, Ni²⁺-responsive probe must typically include aliphatic amines, carbonyls, pyridine, 2,2'-bipyridine or 1,10-phenanthroline in its receptor unit.⁶¹ On the contrary, the ligand field strength has less impact on Ni²⁺ octahedral complexes due to the identical

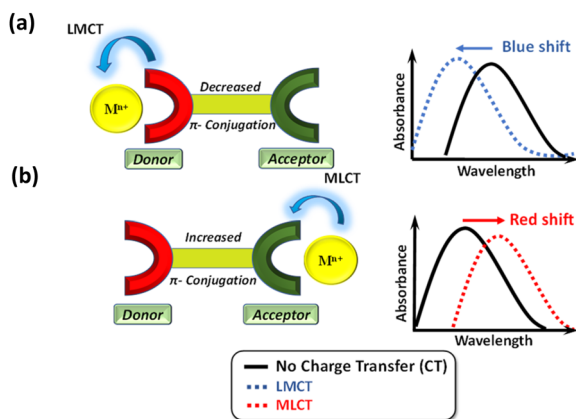


Fig. 2 Distinct binding effects of metal ions on D– π –A system of colorimetric probes with a concomitant shift in UV-Vis spectra due to (a) LMCT and (b) MLCT transitions.

filling of electrons in either low-spin or high-spin d^8 complexes.

(iv) *The hard and soft basicity of donor atoms in the receptor:* the magnitude of the cation–receptor interaction directly depends on both the cation and donor atoms in the receptor. The hard and soft acid and base (HSAB) principle may be implemented to design ideal probes with strong cation–receptor interactions. Ni^{2+} is a borderline (neither hard nor soft) acid, paramagnetic and quite similar in size with neighbouring elements in the periodic table. Therefore, the design of highly selective probes for Ni^{2+} is still a challenging task. Because of its borderline acid character, Ni^{2+} prefers to interact with borderline bases such as imidazole and pyridine donors, tertiary amines, azides, and sulfites. Hence, these groups should be incorporated into the receptor units of Ni^{2+} -responsive probes. Furthermore, to achieve high cation selectivity, the function of solvent and pH of the medium as well as its composition (*e.g.*, presence of competing or interfering species in the medium) should not be ignored. Indeed, a slight change in pH or solvent can remarkably tune or alter the sensing ability of the resultant probe for a particular metal ion.

Finally, to design a metal ion-responsive probe, the ideal situation is to identify a robust binding unit or receptor for the target cation. These receptors typically display the same selectivity to the metal, regardless of the luminophores to which they are tethered. This strategy has been successfully achieved and implemented for some transition metal ions *e.g.*, Cu^+ and Zn^{2+} ions.^{67,90,91} Most of the Cu^+ -responsive probes contain thioether-rich receptors,⁹² while Zn^{2+} could be selectively detected by probes having dipicolylamine (DPA)-based binding motifs.^{93,94} The recognition by these robust receptors enables the development of a library of cation-responsive probes with finely tuned physicochemical and biological properties.

3. Ni^{2+} ion: general features and impact

The industrial demand for nickel (Ni) has dramatically expanded over the last century, resulting in increased pollution and health concerns. Ni^{2+} is utilized in a wide range of metallurgical, environmental, medicines and catalytic processes (*e.g.*, fuel cells, alloys, Ni–Cd batteries, ceramics, dental prostheses, and catalysts).^{52,95,96} However, excess Ni^{2+} in the body can cause allergic contact dermatitis, asthma, conjunctivitis, pneumonitis, lung fibrosis, *etc.* Also, long-term Ni^{2+} exposure (*via* inhalation, dietary intake, water sources, *etc.*) has been linked to cancers of the lungs, nose, sinuses, stomach, and throat.^{17,61,97,98} Although the impact of the Ni^{2+} concentration in living beings is still not fully understood, it is known that excessive Ni^{2+} exposure may generate harmful health consequences. Alternatively, Ni^{2+} is an essential co-factor for many enzymes that play crucial roles in microorganisms (such as bacteria, fungi and algae) and plants.^{99,100} It also participates in various cellular processes, especially energy-related pro-

cesses and nitrogen metabolism. In comparison to other bio-relevant metal ions, the use of Ni^{2+} is found limited but consistent in eukaryotes.¹⁰¹ To date, only a few Ni-containing enzymes such as [NiFe]hydrogenase, urease and Ni-SoD (Ni-superoxide dismutase), have been explored.^{102,103} In contrast, these enzymes are mainly involved in cellular processes of microbes, but no Ni-containing enzyme has been discovered in mammals thus far.^{99,100} Consequently, the detection of Ni^{2+} in the environment and biological systems is critical. Small molecule-based optical sensors can detect and quantify metal ions in a wide range of samples, ranging from cell organelles to all water bodies. Beyond detection, it is also significant and necessary to understand both the physiological and psychological aspects and impacts of Ni^{2+} ions.

4. Metal complex-based sensors

Metal complexes have been extensively investigated for optical sensing of metal ions given that they possess a large Stokes shift, excellent redox and photophysical properties, remarkable photostability and absorption/emission in the visible region.^{56–60} In general, these sensors consist of a ligand system with a single metallic core as the luminophore. To date, most studies on metal complexes as cation-responsive probes have been essentially related to specific transition metals, namely Mn^{2+} , Zn^{2+} , Co^{3+} , Cu^{2+} , and Ru^{2+} complexes.^{104–107} More recently, complexes involving lanthanides (Ln^{3+}) have also emerged as an intriguing alternative in the sensing field.^{108–112} In many cases, the emphasis has been the mechanistic pathway of cation sensing involved in these probes. In these complexes, the receptor is usually linked to the metal core either *via* a σ or π linker. Thus, cation binding to the receptor alters the optical characteristics (luminescence or absorbance) of the corresponding metal complex.¹¹³ In luminescence sensing, this interaction usually allows the metal complex to serve as either a ‘turn-on’- or ‘turn-off’-type sensor. The binding unit having conjugation with the metal core *via* a π linker may also lead to a change in the emission wavelength of the metal complex upon target binding. Alternatively, the colorimetric sensors display a color change upon the addition of the analyte.¹¹⁴

4.1 Luminescent Ni^{2+} sensors

The development of new luminescent sensors for the quick and easy detection of Ni^{2+} is appealing. To the best of our knowledge, the first report on a metal-based receptor for the luminescence sensing of Ni^{2+} ions was presented by Bolletta *et al.* in 1999.¹¹⁵ In their study, a Ru^{2+} (bpy) complex (**1**) based on a dioxo-tetramine ligand (*i.e.*, tetra-aza macrocycle) acted as a luminescent probe for Cu^{2+} and Ni^{2+} ions in aqueous medium (Fig. 3). The sensing ability of probe **1** was assessed by monitoring the alterations in its luminescence intensity and excited-state lifetime as a function of pH, with and without Ni^{2+} ions. In the absence of Ni^{2+} , the luminescence intensity of probe **1** remained constant in the pH range of

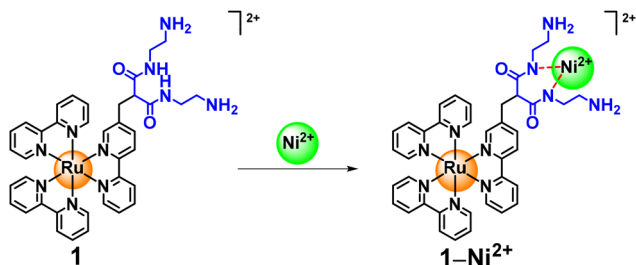


Fig. 3 Binding mode of Ru²⁺-based probe 1 towards Ni²⁺ in aqueous phase.

2.0–12.0. In this pH range, the emission quantum yield ($\Phi_{em} = 0.030$) and the excited-state lifetime ($t = 440$ ns) of **1** were similar to that found for the prototype complex, *i.e.*, [Ru(bpy)₃]²⁺, in aqueous medium. These results clearly indicated that the dioxo-tetramine ligand showed no remarkable perturbation to the excited-state characteristics of the Ru²⁺-bpy fragment. On the contrary, upon the addition of Ni²⁺ ions to **1** in a 1:1 molar ratio, a typical sigmoidal profile was observed in the plot of luminescence intensity *vs.* pH of the medium. The decrease in the excited-state lifetime to 11.0 ns clearly indicated the strong intramolecular luminescence quenching of probe **1** in the presence of Ni²⁺ ions. The authors anticipated that the luminescent intensity was quenched due to the energy transfer process with a steady-state quenching constant of 2.1×10^7 s⁻¹.

Later, in 2009, Mukherjee's group¹¹⁶ developed luminescent molecular rectangle **2** for potential applications toward cation recognition (Fig. 4). The four N atoms from the imine (–CH=N–) groups in the core enable probe **2** to act as a suitable receptor for moderately hard transition metal ions such as Ni²⁺, Cu²⁺, and Mn²⁺. The 1,8-platinum-functionalized anthracene units were referred to as 'molecular clips', and the presence of the ethynyl functionality in the structure of the probe induced the luminescence behavior of the luminophore

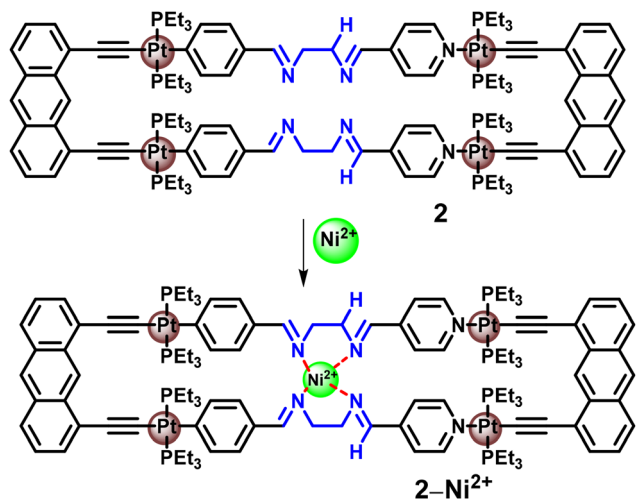


Fig. 4 Binding mode of Pt-based probe **2** towards Ni²⁺ in methanol.

in this probe. The UV-Vis spectrum of **2** in methanol displayed an intense absorption peak at 258 nm, which was ascribed to the intraligand $\pi \rightarrow \pi^*$ transition. In addition, low-intensity absorptions were also observed at 424 nm, 400 nm, 380 nm and 353 nm. Upon excitation with 400 nm light, probe **2** emitted at approximately 460 nm in methanol (*ca.* 3.0×10^{-5} M). The luminescence intensity of **2** was significantly quenched upon titration with Cu²⁺ and Ni²⁺, exhibiting PeT as the possible mechanistic pathway for the quenching event. Interestingly, the luminescence of **2** could easily be revived with the addition of 2,2'-bipyridine to a solution of the 2-Ni²⁺ adduct.

In the subsequent year, probe **3** was reported by Li *et al.*,⁴⁶ which was the first metal-based probe exclusively selective for Ni²⁺ ions (Fig. 5). This probe was comprised of a Zn²⁺-based coordination compound with a multifunctional symmetrical Schiff base as the ligand scaffold. The emission of this probe could be seen at 363 nm when excited at 295 nm in 10⁻⁵ M DMF (*N,N'*-dimethylformamide) solution. The addition of 1.0–3.0 equiv. of Ni²⁺ resulted in an enhancement in the luminescence of probe **3**, whereas its luminescence decreased in the presence of other metal ions, *e.g.*, Cu²⁺, Mn²⁺, Al³⁺, K⁺, Mg²⁺, Cd²⁺ and Na⁺ ions. The binding of Ni²⁺ to **3** was further supported by the single-crystal X-ray diffraction (SC-XRD) study, leading to the description of 3-Ni²⁺ as a heterometallic trinuclear compound. The authors anticipated that the incorporation of two Ni²⁺ ions provided additional rigidity to the probe, which reduced the energy loss occurring due to vibrational motions.

In the same year (2012), the Tian, Sun and group⁴⁸ constructed a ligand in which a terpyridine (tpy) unit was linked with a triazole unit through a phenyl linker (Fig. 6). It is well known that the tpy moiety displays relatively stronger binding with borderline acids such as Zn²⁺ compared to the triazole unit. Consequently, the treatment of this ligand with a Zn²⁺ salt afforded the formation of complex **4** having two tpy units coordinated to the metal centre. The crystal structure analysis of **4** clearly revealed that the tpy rings slightly deviated from the plane of the phenyl linker, ultimately resulting in intense luminescence and efficient energy transfer process. The luminescence sensing ability of **4** towards different metal ions was carried out in DMF solution. Other metal ions such as

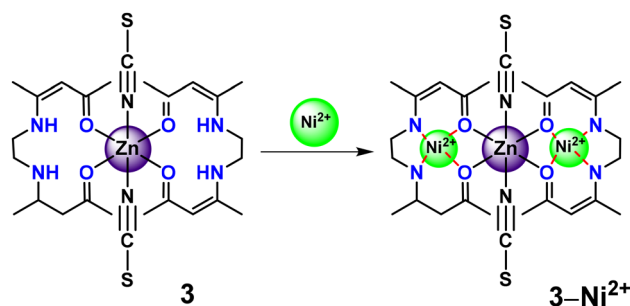


Fig. 5 Binding mode of Zn-based supramolecular probe **3** with Ni²⁺ in DMF solution.

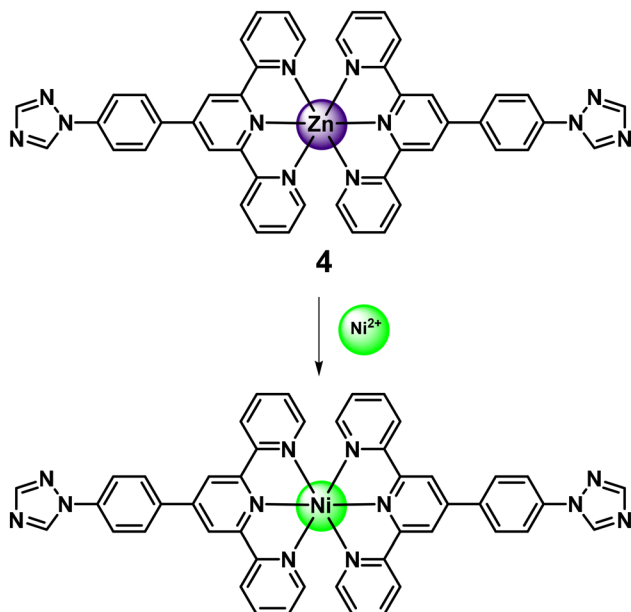


Fig. 6 Detection of Ni²⁺ ions by the displacement of the central atom in Zn-based probe 4.

Fe^{2+/3+}, Cu²⁺, Zn²⁺, Cd²⁺ and In³⁺ induced a small emission quenching at 360 nm ($\lambda_{\text{ex}} = 291$ nm), which could be attributed to either the paramagnetic nature of the related metals or electron/energy transfer processes. On the contrary, Co²⁺ and Ni²⁺ ions triggered the complete luminescence quenching of probe 4. ESI-MS measurements were performed to gain better insight into the luminescence quenching caused by the addition of Ni²⁺ ions. The molecular ion peak of [Zn(L)₂]²⁺ at *m/z* 408.28 disappeared in the ESI mass spectrum of 4-Ni²⁺; however, a new peak at *m/z* 405.33 corresponding to [Ni(L)₂]²⁺ appeared. It was suggested that Ni²⁺ and Co²⁺ ions could replace Zn²⁺ in 4 and bind strongly with the tpy unit, leading to complete luminescence quenching, whereas weak coordination of the triazole unit could be realized in the case of other metals. Furthermore, the luminescence of probe 4 could not be revived upon the addition of EDTA (ethylenediaminetetraacetic acid), indicating the strong affinity of the tpy moiety for the Ni²⁺ ion.

In 2018, Baitalik's group¹¹⁷ developed two bis-tridentate Ru (ii) probes 5 and 6 based on tpy derivatives as ligands to investigate their cation-responsive behaviors (Fig. 7). The main ligand frame consisted of a tpy moiety linked with a pyridine-imidazole group *via* a phenyl linker. The absorption and emission spectra of 5 and 6 were recorded in different organic solvents such as dichloromethane (DCM), methanol, ethanol, acetonitrile (ACN or CH₃CN) and dimethylsulfoxide (DMSO), and the comprehensive spectral features of these probes were discussed in detail. The UV-Vis spectra of 5 and 6 displayed sharp bands in the range 230–293 nm due to the ligand centred $\pi \rightarrow \pi^*$ transition while a metal-to-ligand-charge-transfer (MLCT) band was observed between 491 nm and 508 nm. In addition, one intraligand charge transfer (ILCT) band was

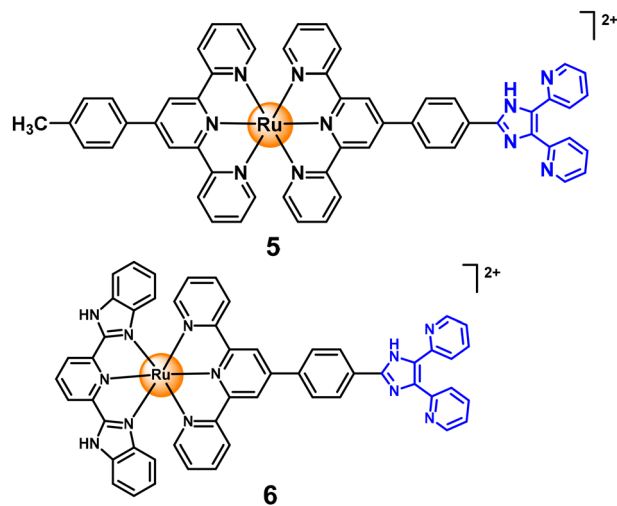


Fig. 7 Chemical drawings of probes 5 and 6.

noticed between 311 nm and 354 nm in the UV-Vis spectra of both 5 and 6. The emission maximum was observed at 660 nm for 5 and 688 nm for 6 when excited at 490 nm in DMSO solution. Both probes exhibited emission at room temperature and at low temperature (77 K), having excited-state lifetimes in the range of 0.5 to 70.0 ns (nanoseconds), eventually relying on the solvent as well as the co-ligands. The spectral changes in the absorption and emission spectra of the probes were monitored in the presence of various metal ions such as Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Cd²⁺ and Hg²⁺ in CH₃CN solution. The MLCT band remained intact in both probes upon the addition of Mn²⁺, Pb²⁺, Co²⁺, Cd²⁺ and Hg²⁺, whereas a small decrease in its intensity was observed for Ni²⁺, Fe²⁺ and Cu²⁺ ions. Notably, the absorption intensity of the ILCT band increased, in general, with the level of increase varying depending on the cations studied. Among the various metal ions, a very small luminescence enhancement was observed with Zn²⁺ for both probes, most probably due to the PeT process. The emission behavior of 5 and 6 remained roughly unaltered with Pb²⁺, Hg²⁺ and Cd²⁺ ions, whereas remarkable quenching appeared in presence of Fe²⁺, Ni²⁺ and Cu²⁺ ions.

Later, in 2021, Cui's group^{118,119} developed two Co(II)-based luminescent probes, [Co₂(L₁)(NPTA)]·H₂O (7) and [Co(L₂)(nph)]·*n*H₂O (8) (where L₁ and NPTA represent 1,2-bis(thiabendazole-1-ylmethyl)benzene and 2-nitroterephthalic acid; L₂ and nph represent 1,1'-(1,6-hexanediyl)bis[2-(2-pyridyl)benzimidazole] and 3-nitroterephthalic acid, respectively), as Ni²⁺ receptors. The crystal structures of both 7 and 8 were depicted by SC-XRD study (Fig. 8). The luminescence behaviors of these probes towards various cations and anions were investigated in the solid-state and solution phase at room temperature. The emission maximum for 7 and 8 was centred at 378 nm ($\lambda_{\text{ex}} = 298$ nm) and 381 nm ($\lambda_{\text{ex}} = 299$ nm), respectively, in the solid-state at room temperature. The dispersion of probe 8 in water did not display any change in its luminescence intensity even after 100 min, which suggested the stable nature of this probe in aqueous media. The luminescence intensity of probe 8 was

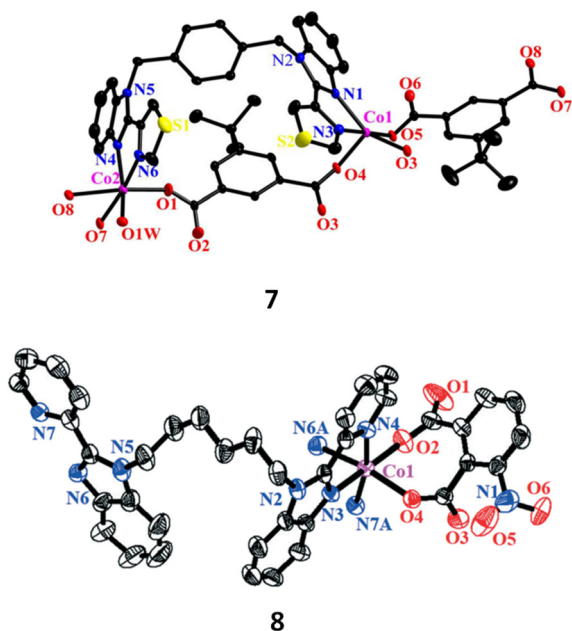


Fig. 8 Crystal structures of probes 7 and 8. Adapted with permission from ref. 118. Copyright 2021, The Royal Society of Chemistry, and ref. 119, Copyright 2021, Springer.

highly influenced by diverse cations; however, substantial quenching (*ca.* 93%) was noticed solely for the Ni^{2+} ion. The selectivity studies exhibited that the quenching effect for Ni^{2+} was not interfered by other metal ions (such as K^+ , Ag^+ , Mg^{2+} , Al^{3+} , Ca^{2+} , Co^{2+} , Zn^{2+} , Sr^{2+} , Cd^{2+} , Hg^{2+} , Cr^{3+} , Fe^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} and Er^{3+}), and thus 8 displayed excellent selectivity for Ni^{2+} ions with an LoD value of $4.54 \mu\text{M}$. Probes 7 and 8 were also explored for their sensing ability towards anionic species. Interestingly, 7 showed a selective luminescence response towards MnO_4^- over several competing anions (*e.g.*, Cl^- , Br^- , I^- , ClO_3^- , BrO_3^- , IO_3^- , NO_3^- , OCN^- , MnO_4^- , SCN^- , CO_3^{2-} , SO_4^{2-} , $\text{H}_2\text{PO}_4^{2-}$, HPO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ and $\text{P}_2\text{O}_7^{4-}$) with a remarkable quenching efficiency of *ca.* 97%. The emission decay lifetimes of 7 and 8 were depicted to be $1.737 \mu\text{s}$ and $3.837 \mu\text{s}$, respectively, as evidenced by the bi-exponential fitting of the luminescence decay data. The luminescence quenching in 7 or 8 was attributed to either a photoinduced e^- transfer from the probe to Ni^{2+} (host to guest) or the competitive absorption of excitation light between 7/8 and the target Ni^{2+} ion.

Later, in the same year (2021), Han and group¹²⁰ reported a water-soluble zinc(II)-based coordination compound 9 that could detect Fe^{3+} , Cu^{2+} , Ni^{2+} and CrO_4^{2-} ions among diverse panels of cations and anions (Fig. 9(a)). Probe 9 exhibited its emission maximum centred at 371 nm upon excitation at 335 nm in water. Among the various cations studied, Fe^{3+} induced the maximum luminescence quenching in 9 at 371 nm, which was ascribed to the energy transfer and competitive wide absorption spectrum (200–400 nm) of the source, whereas the quenching mechanism of Ni^{2+} and Cu^{2+} ions was ascribed to the overlap of the excitation spectrum of the probe and the absorption of the cations studied (Fig. 9(b)). The

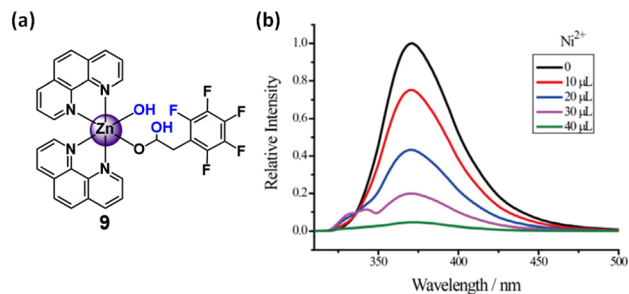


Fig. 9 (a) Chemical drawing of probe 9 and (b) luminescent quenching of 9 upon addition of Ni^{2+} ions in water. Adapted with permission from ref. 120. Copyright 2021, Elsevier.

Stern–Volmer constant (K_{sv}) value for Ni^{2+} was $2.68 \times 10^4 \text{ M}^{-1}$ with the LoD of $0.491 \mu\text{M}$.

4.2 Colorimetric Ni^{2+} sensors

In an elegant study in 2004, Stang and co-workers¹²¹ constructed supramolecular rectangular probe 10 for the rapid optical-based detection of Ni^{2+} , Cd^{2+} and Cr^{3+} ions in methanolic solution (Fig. 10). UV-Vis spectroscopy was employed to test the cation sensing ability of this probe. The absorption spectrum of 10 in methanol exhibited three major bands centred at 230 nm, 280 nm and 350 nm. Upon the addition of Ni^{2+} to the probe solution, remarkable changes were observed in the absorption spectrum of 10, with one isosbestic point noticed at 300 nm. A 1 : 1 binding stoichiometry for the formation of complex 10- Ni^{2+} was evidenced by the Job's plot and ESI mass analyses, and the binding constant was determined to be $2.01 \pm 0.05 \times 10^7 \text{ M}^{-1}$.

In 2012, Molina, Tàrraga and co-workers⁴⁷ reported a series of unsymmetrical di-substituted ferrocenes (11–13) containing triazole units developed using the Staudinger–aza Wittig

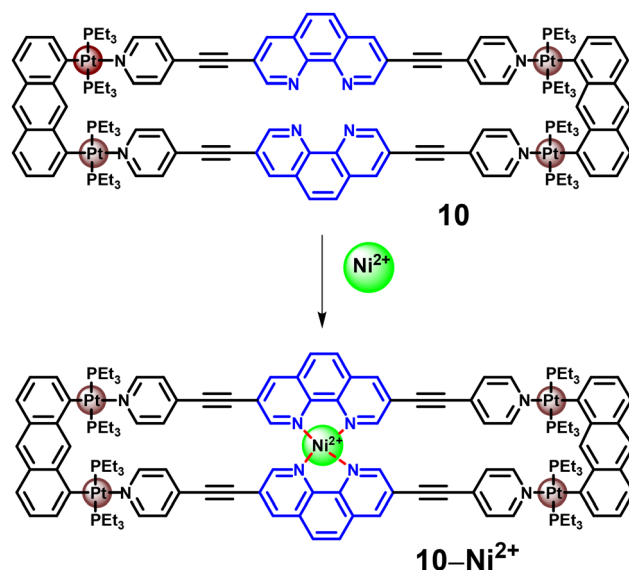


Fig. 10 Binding mode of Pt-based probe 10 towards Ni^{2+} in methanol.

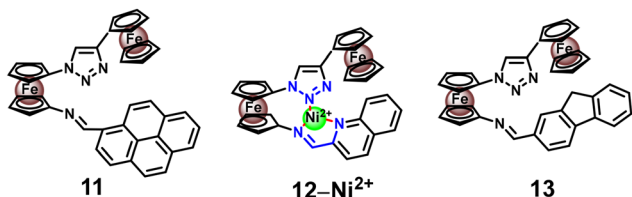


Fig. 11 Chemical structures of probes **11–13**, and binding mode of **12** with Ni^{2+} ions.

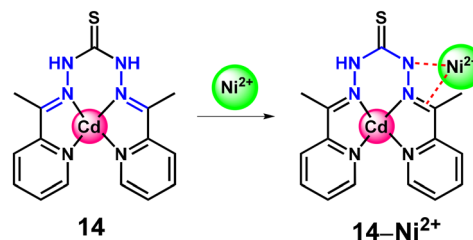


Fig. 12 Binding mode of Ni^{2+} with Cd(II)-based probe **14**.

process (Fig. 11). These complexes were explored as optical probes to detect various metal ions. Among the reported probes, **12** acted as a colorimetric sensor for Ni^{2+} and Cd^{2+} ions. The crystal structure of **12** was elucidated by SC-XRD analyses, exhibiting a monoclinic space group Cc , which was further corroborated with the help of DFT studies. UV-Vis spectroscopy displayed a high energy absorption band centred at 284 nm for **11**, 317 nm for **12**, and 336 nm for **13** in a mixture of organic solvents ($\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$). Two low energy bands responsible for the red color of the probes could also be seen in the range of 317–380 nm and 479–495 nm. These probes showed a half-wave potential value of $\Delta E_{1/2} = 0.02$ V, $\Delta E_{1/2} = 0.26$ V, and $\Delta E_{1/2} = 0.21$ V for **11**, **12**, and **13** (Fc^+/Fc redox couple), respectively, with two reversible redox waves of one-electron. The redox potential of **11** and **13** was affected only by the addition of Pb^{2+} and Zn^{2+} ions among the investigated cations (*i.e.*, Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Hg^{2+} , and Cu^{2+}). However, metal ions such as Ni^{2+} , Cd^{2+} , Zn^{2+} , and Pb^{2+} remarkably altered the redox potential of **12**. The response of these cations towards **12** was further investigated by UV-Vis studies in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ solution, where significant changes were observed after the addition of Ni^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+} ions. Probe **12** displayed a large shift in its absorption band, *i.e.*, 110 nm, upon the addition of Ni^{2+} and Cd^{2+} ions with a change in the color of the probe solution from red to blue (visible to the naked eyes), together with two clear isosbestic points. The Job's plot analysis further indicated a 2 : 1 binding ratio for Ni^{2+} and Cd^{2+} with the association constant values of $1.4 \times 10^{10} \text{ M}^{-2}$ and $4.8 \times 10^9 \text{ M}^{-2}$ and the limit of detection (LoD) of $8.7 \times 10^{-7} \text{ M}$ and $2.8 \times 10^{-6} \text{ M}$, respectively. Zn^{2+} and Pb^{2+} showed distinctive spectral changes but no color change was observed in these cases. The emission of probe **12** was suppressed due to the presence of triazole and ferrocene units ($\phi_{\text{em}} = 0.001$); however, the addition of only Zn^{2+} resulted in a slight enhancement in its emission band ($\phi_{\text{em}} = 0.006$). Electrospray ionization mass spectroscopic (ESI-MS) analysis of **12** in the presence of Ni^{2+} and Cd^{2+} exhibited 1 : 1 fragments with $[\text{12-CdClO}_4]^+$ (m/z 803) and $[\text{12-NiClO}_4]^+$ (m/z 747), respectively.

In the same year (2021), Hishimone *et al.*¹²² reported Cd²⁺-based probe **14** with a thiosemicarbazone group in the ligand framework (Fig. 12). In DMF solution, the UV-Vis studies for **14** revealed a high-intensity ILCT band centred at 410 nm together with a low-intensity MLCT band near 535 nm. A moderate-intensity absorption was also observed at 306 nm, which

is most likely due to the LC $\pi \rightarrow \pi^*$ transition. The nitrate salts of cations such as Fe^{3+} , Ag^+ , Zn^{2+} , Mn^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Cr^{3+} , Pb^{2+} and Hg^{2+} were added to the probe solution, and the changes in its absorption spectrum were monitored. Upon the addition of Ni^{2+} ions (5.0 equiv.) to the probe solution (*ca.* 10^{-5} M) in DMF, the ILCT band at 410 nm decreased, and concomitantly a new band appeared near 500 nm, which suggested the formation of a new species. An isosbestic point was also observed at 437 nm with a substantial change in the color from yellow to brown (obvious to the naked eyes). Other metal ions such as Cu^{2+} , Co^{2+} and Hg^{2+} produced similar changes in the absorption spectra with a similar colorimetric response. The formation of adduct **14-Ni**²⁺ was also corroborated by ESI-MS and NMR analyses. No changes in the spectra were observed upon introducing anionic species such as F^- , OH^- , CN^- , AcO^- , Cl^- , Br^- , I^- and HSO_4^- ions. The binding constant and LoD values for **14-Ni**²⁺ were computed to be $1.55 \times 10^2 \text{ M}^{-1}$ and $1.30 \times 10^{-10} \text{ M}$, respectively.

5. MOF-based sensors

Metal-organic frameworks (MOFs) are inorganic-organic hybrid materials typically assembled by metal ions/metal clusters and suitable organic ligands through coordinate bonds to form one-, two-, or three-dimensional structures.^{123,124} The appropriate selection of organic compounds and metal ions plays a crucial role in the design and development of MOFs. Distinctively from traditional solid-state porous materials, *e.g.*, zeolites, molecular sieves and activated carbons, MOFs display some unique structural features mainly due to their open porous structure, remarkable porosity, large surface area, and tuneable pore surface.^{125,126} These intrinsic characteristics have facilitated the application of MOFs in different fields including gas adsorption/separation,^{127,128} magnetic materials,^{129,130} drug delivery,^{131,132} heterogeneous catalysis,^{133,134} and optical devices.^{135,136} Amongst them, the use of MOFs as luminescent or colorimetric sensing materials to detect various analytes (such as cations, anions, and neutral molecules) constitutes one of the most important applications. Hence, over the years, a diverse panel of luminescent MOF-based probes have been developed to detect metal ions, anions, small gases, organic molecules, *etc.*,^{137–139} while MOFs substantially acting as colorimetric sensors are relatively less explored.

The following section only covers MOFs acting as optical probes specifically for the detection of Ni²⁺ ions. Thus far, most of the studies on MOFs as luminescent probes for detecting Ni²⁺ have been mainly related to Zn²⁺- and Cd²⁺-based metallic cores. More recently, MOFs involving lanthanide ions have also emerged as an intriguing alternative in the sensing field.

5.1 Luminescent Ni²⁺ sensors

In 2015, Wang *et al.*¹⁴⁰ reported cadmium-based MOF **15** as a luminescent probe to detect Ni²⁺ in *N,N*-dimethylacetamide (DMA) solution. Probe **15** was comprised of non-interpenetrating pillar-layers bearing 5-aminoisophthalic acid and 3,5-(dipyridin-4-yl)-4*H*-1,2,4-triazol-4-amine groups as organic ligands. Recently, pillar-layer MOFs have attracted significant attention from researchers due to their following key features: (i) a variation in the length of the pillar linkers may tune the shape and size of the pores with a negligible change in the structural topology of the MOF and (ii) the direct functionalization of the pillar linkers may result in a variation in the hydrogen bonding and hydrophobic/hydrophilic character of the MOF. Accordingly, 3,5-(dipyridin-4-yl)-4*H*-1,2,4-triazol-4-amine was chosen as the organic linker due to its extended π -conjugated feature to improve the luminescent character of the resultant MOF. Moreover, the Cd²⁺ ion was selected to construct the metallic core in probe **15** due to its multiple coordination numbers and promising photophysical properties. A pentagonal bi-pyramidal geometry was adopted by Cd²⁺ bearing five oxygen atoms at the equatorial positions and two nitrogen atoms at the axial positions (Fig. 13). To determine its sensing ability for cations, a DMA solution of different metal salts, *e.g.*, Cd²⁺, Co²⁺, Ag⁺, Ni²⁺ and Zn²⁺ (*ca.* 10⁻² M) was individually introduced in a DMA solution of probe **15**. A luminescence enhancement in the intensity of **15** at 410 nm could be realized in the case of Cd²⁺, Zn²⁺ and Ag⁺, most likely due to their closed-shell electronic configuration. In contrast, Co²⁺ and Ni²⁺ induced luminescence quenching with the most

significant decline in the case of Ni²⁺. The largest enhancement (*ca.* 8.0-fold) observed for Cd²⁺ was attributed to the bridging effect, which enhances the conjugation and the rigidity of the probe, while the quenching in the case of Ni²⁺ was ascribed to the reduction in the intraligand luminescence efficiency *via* weak binding between Ni²⁺ and the nitrogen atoms.

In the same year, another Cd²⁺-based probe, **16**, was synthesized by Feng and co-workers¹⁴¹ for the recognition of Ni²⁺ in aqueous solution. The 5-(4-carboxybenzyloxy)-isophthalic acid ligand was chosen as the bridging group due to the presence of three carboxylate (–COO[–]) moieties in this ligand, which may ultimately lead to diverse bridging modes to be adopted in the construction of the MOF. The solid-state luminescence behavior of **16** was investigated at room temperature. The emission maximum was observed near 443 nm when excited at 368 nm and was attributed to the ligand-to-metal-charge-transfer (LMCT) transition. The luminescence sensing ability of **16** for different metal ions such as K⁺, Co²⁺, Ni²⁺, Zn²⁺, Cu²⁺, Ba²⁺ and Pb²⁺ was studied in aqueous solutions. Quenching of the emission band at 443 nm was observed in the case of Cu²⁺, Ba²⁺, Co²⁺, Zn²⁺ and Ni²⁺, with the most significant effect for Ni²⁺, which is most probably due to the strong coordination of Ni²⁺ with the free carboxylate moieties.

In lanthanide chemistry, the Ln(III) f–f transitions are Laporte forbidden, typically resulting in low absorption coefficients, and thus the photophysical characteristics of Ln(III) are dependent on the coordinating environment of Ln(III). Thus, to overcome this inherent obstacle, an appropriate organic ligand displaying the ‘antenna effect’ (*vide supra*) is usually incorporated in the Ln(III) centre.^{142–144} An alternative to improve the emission of Ln(III) is to incorporate a d-block metal complex (transition metal complex) as sensitizer for the lanthanide emission. To engineer the latter, a suitable organic ligand is typically chosen to bridge the d-block metal-based chromophore and the Ln(III)-based luminophore into d–f heterobimetallic species. Subsequently, the sensitized luminescence of the Ln(III) is achieved *via* d → f energy transfer. The d-block chromophore employed with Ln(III) may enhance or quench the luminescence of Ln(III), relying on either d → f or f → d energy transfer, respectively.^{145–147} However, most of the works reported thus far are limited to the development of bimetallic 3d–4f, 4d–4f or 5d–4f species.

To further extend this concept, in their elegant study, Wang *et al.*¹⁴⁸ developed two structurally similar Yb(III)–Cd(II)–Mn(III)- and Yb(III)–Cd(II)–Zn(II)-based luminescent MOFs **17** and **18** bearing oxidiacetic acid as the ligand, respectively (Fig. 14). This was the first report representing a mixed 4f–4d–3d framework exhibiting selectivity towards Ni²⁺ ions. The authors anticipated that the direct interaction of the 3d or 4d orbitals of transition metal ions with the 4f orbital of Yb(III) may tune the energy of the 4f level, resulting in a variation in the luminescence performance of Yb(III). After excitation at 360 nm, a narrow sharp band was observed between 975 nm and 1025 nm with the emission maximum centred at 998 nm

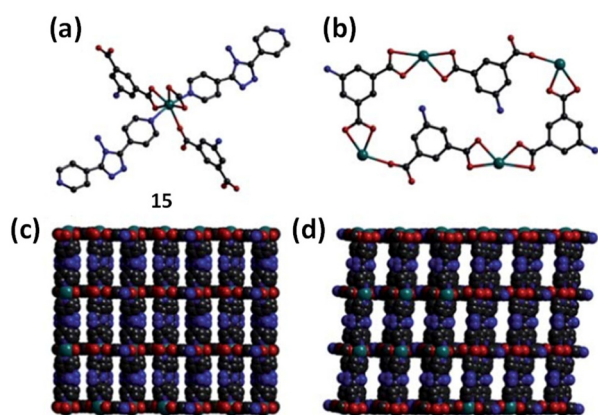


Fig. 13 (a) Coordination environment of cadmium centre in probe **15** [Cd, teal; C, black; O, red; and N, blue] and (b) macrometallocycles. (c) & (d) Channel representation of probe **15**. Adapted with permission from ref. 140. Copyright 2015, The Royal Society of Chemistry.

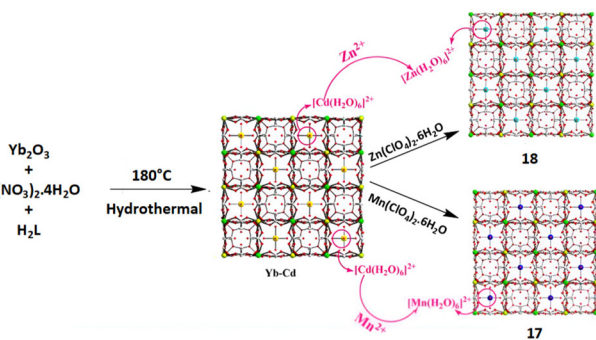


Fig. 14 Synthesis of trimetallic MOF probes **17** and **18**. Adapted with permission from ref. 149. Copyright 2015, American Chemical Society.

in DMF solution. This emission band was assigned to the Yb(III)-based ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition. Probe **17** exhibited a luminescence quenching response at 995 nm in the presence of Ca^{2+} , Mg^{2+} , Ni^{2+} or Zn^{2+} and drastic quenching could be observed in the case of Cd^{2+} or Co^{2+} in DMF solution. Conversely, probe **18** showed a remarkable luminescence enhancement at 998 nm when Ni^{2+} ions were added to it, while the intensity of this peak was diminished in the presence of Ca^{2+} , Co^{2+} and Mg^{2+} ions. The luminescence enhancement was attributed to the changes in the excited-state level of the Cd^{2+} moiety, which transferred energy more efficiently to the Yb^{3+} ions.

In 2016, a series of isostructural Ln(III)-based 1D polymeric materials equipped with tetrafluorophthalic acid and 1,10-phenanthroline as ligands was demonstrated by Li and group.¹⁴⁹ Among the different Ln(III) ions including Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III), only probe **19** involving Eu(III) was reported to have selectivity towards nitrobenzene and Ni^{2+} ion. The characteristic emission bands for Eu^{3+} were observed at 594 nm, 614 nm, 651 nm and 683 nm due to the ${}^5D_0 \rightarrow {}^7F_J$ transitions (where $J = 1-4$). The strongest transition, *i.e.*, ${}^5D_0 \rightarrow {}^7F_2$, was attributed to the electronic dipole transition, which is responsible for the characteristic red color of Eu^{3+} . This probe displayed a luminescence lifetime of 0.5565 ms with an emission quantum yield of 15.87%. A suspension was observed after the dispersion of **19** in an aqueous solution of various metal ions. A variable degree of emission quenching was exhibited by Na^+ , Cd^{2+} , K^+ , Li^+ , Al^{3+} , Ca^{2+} and Ni^{2+} , whereas Mg^{2+} and Pb^{2+} ions caused a slight change in the emission. The most pronounced effect was noticed in the case of Ni^{2+} , where 1.0 mmol L^{-1} Ni^{2+} ions induced significant emission quenching (*ca.* 90%) at 615 nm. Upon the progressive addition of Ni^{2+} (up to 10.0 mmol L^{-1}) to **19**, its emission band was almost completely quenched (approx. 99%). This quenching behavior was attributed to the partially filled d-subshell of the target ions. This MOF was also robust enough and showed identical results for Ni^{2+} and nitrobenzene even after five cycles.

In the same year (2017), Zheng *et al.*⁵⁰ presented a series of Ln-MOFs with 1,3-adamantanediacyetic acid and 1,10-phenanthroline as ligands. Probe **20** having Eu as the metallic core exhibited the characteristic emission bands for the Eu^{3+} ion at

576 nm, 592 nm, 613 nm, 650 nm, and 698 nm, corresponding to the ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0$ to 4) transitions, respectively. The lifetime of probe **20** was reported to be 1.478 ms with a quantum yield of 58.61%. Interestingly, the Tb^{3+} analogue of probe **20** displayed a much lower quantum yield (9.07%), which suggested that the phen moiety transfers energy more preferably to the Eu^{3+} ion than to the Tb^{3+} ion. Probe **20** exhibited luminescence quenching in the presence of Ni^{2+} in water, while other metal ions such as Mn^{2+} , Co^{2+} , Cd^{2+} , Ba^{2+} , Zn^{2+} , Pb^{2+} , Cr^{3+} , Fe^{2+} and Mg^{2+} resulted in negligible changes in its emission spectrum. Moreover, among the different amino acids tested, the addition of valine resulted in drastic enhancement in the emission intensity of **20**. This probe had a low LoD value of $1 \times 10^{-9} \text{ M}$; however, a significant interference was experienced from Cd^{2+} , Mg^{2+} , Co^{2+} , Mn^{2+} , Val and Trp. The quenching mechanism was explained based on the LMCT after the addition of Ni^{2+} ions, which interrupts the antenna effect. The other analogues of **20** with Gd^{3+} , Tb^{3+} , La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , and Y^{3+} displayed no selectivity or sensitivity to Ni^{2+} ions. Later, in 2018, Wu and co-workers¹⁵⁰ developed luminescent probe **21**, a cyclopentanedicarboxylic acid and Zn^{2+} -based coordination polymer. The narrow emission maximum of **21** was observed at 584 nm in phosphate buffered saline (PBS) solution. This probe showed a high degree of quenching upon the addition of Ni^{2+} ions, while other ionic species such as Al^{3+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Mg^{2+} , Mn^{3+} , Pd^{2+} , Zn^{2+} , Na^+ , K^+ , NH_4^+ , NO_3^- , and Cl^- failed to cause any changes in its emission intensity. Slight quenching was also observed in the case of Fe^{3+} and Cu^{2+} but the response was nominal in comparison to that for Ni^{2+} . Metal ions such as Fe^{3+} and Cu^{2+} ions did not interfere in the selective detection of Ni^{2+} ions, which is a key parameter to utilise **21** for practical applications in real specimens. The influence of temperature and pH on the luminescence behavior of this probe was also studied. The authors reported that the optimal pH was in the range of 4.0–6.0, and the luminescence intensity was reduced by 34.5% when the temperature was increased from 25 °C to 50 °C. Probe **21** was also tested in real samples such as filtered lake water using PBS buffer solution (pH 7.0). Six different samples were taken from the Songshan Lake. Initially, the solutions were filtered to remove any insoluble earthy bulk materials, followed by the addition of PBS buffer to maintain the pH of 7.0. The excellent recoveries of 99% to 104% with the relative standard deviation of 3.0% suggested the potential utility of this MOF as a chemosensory probe in environmental settings. The Stern–Volmer constant of $5.74 \times 10^5 \text{ L mol}^{-1}$ with a bimolecular quenching constant of $5.47 \times 10^{13} \text{ L mol}^{-1} \text{ s}^{-1}$ indicated a static quenching mechanism and a remarkable soft acid–base interaction between Ni^{2+} and carbonyl groups. The LoD value for Ni^{2+} was calculated to be $5.23 \times 10^{-7} \text{ mol L}^{-1}$ in this study.

Later, Cu^{2+} -based MOF **22** containing 2-aminobenzene-1,3,5-tricarboxylate as the organic linker was designed by Rubin *et al.* in 2019 (Fig. 15(a)).¹⁵¹ The emission spectrum of **22** displayed a band near 400 nm in DMF solution. To investigate the sensing behavior of **22** for different cations, a 10 mM solution of various metal ions was added to 2 mg of finely dis-

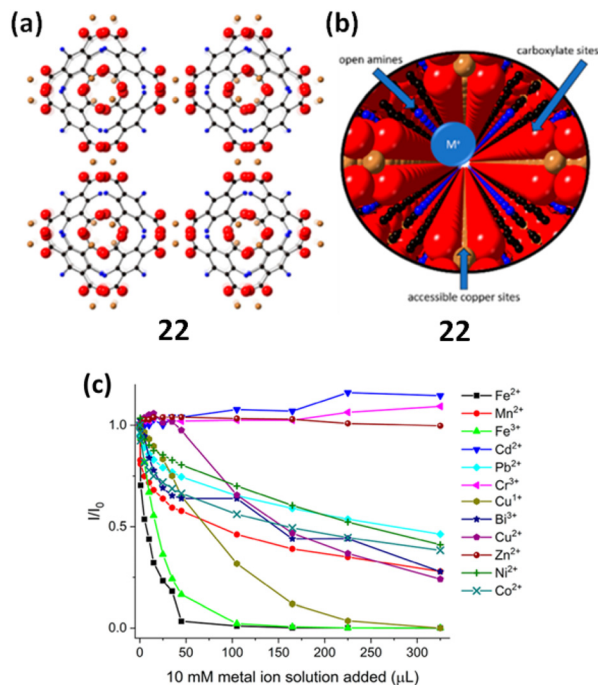


Fig. 15 (a) Secondary-building-unit (SBU) of probe 22 having available functionalities such as amines (in blue color), carbon (in black color), oxygen (in red color) and Cu (in tan color). (b) Space-filling model exhibiting the possible interaction site for the guest metal ion in the framework and (c) normalized emission intensity (I/I_0 , where $\lambda_{em} = 400$ nm and $\lambda_{ex} = 350$ nm) of probe 22 in the presence of 10 mM of different metal ions. Adapted with permission from ref. 151. Copyright 2019, the American Chemical Society.

persed 22 in DMF, which was shaken for 30 s and sonicated for 1 h. The emission spectrum of 22 exhibited complete quenching upon the progressive addition of Fe²⁺ and Fe³⁺ (1.55 to 56.0 ppm). Noticeable quenching was also reported for Pb²⁺, Cu²⁺, Mn²⁺, Ni²⁺ and Co²⁺ with a detection limit of 5.7, 12.0, 3.0, 1.6 and 0.2 ppm, respectively (Fig. 15(c)). Also, 22 was found to be sensitive to anions such as CO₃²⁻, AcO⁻ and Cr₂O₇²⁻, whereas other common anions such as Cl⁻, Br⁻, I⁻ and NO₃⁻ caused nominal changes. The diverse sensing behavior of this MOF was demonstrated by the HSAB theory. According to the HSAB principle, the luminescence quenching was observed by either borderline hard acids, e.g., Bi³⁺, or soft acids such as Cu⁺, whereas the hard acids, e.g., Cr³⁺, showed no remarkable change in emission intensity. Furthermore, alkali metals showed a nominal change in the spectrum, whereas alkaline earth metals exhibited ca. 50% luminescence quenching with the appearance of a new peak at 475 nm. The authors anticipated that the interaction of a molecule in the excited-state with a nearby non-excited molecule may lead to the changes observed in the luminescence profiles. The reason for the observed luminescence quenching was attributed to the blockage of the free amine group induced by the guest analyte in the probe.

In the subsequent year (2020), Qin *et al.*⁵¹ synthesized the highly luminescent probe 23, a Zn²⁺-based MOF bearing 4,4'-

oxybis-(benzoic acid) and 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole as the organic linkers. Three metal centres were linked by the SO₄²⁻ ion to give a tri-metallic node acting as a secondary building unit (SBU) in probe 23. Finally, a 2D tripillared-bilayer structure could be obtained *via* the linking between the SBU and the ligands. The emission spectrum of 23 showed an intense band near 474 nm when excited at 310 nm. To investigate the cation sensing ability of 23, it was soaked in a 10 mM aqueous solution of different metal ions such as Na⁺, K⁺, Mg²⁺, Al³⁺, Pb²⁺, Co²⁺, Ni²⁺, Cd²⁺, Zn²⁺, Mn²⁺ and Cr³⁺. Subsequently, the guest-containing solutions were filtered and dried and their luminescence spectra recorded. Among the various metal ions tested, Ni²⁺ caused the strongest luminescence quenching (ca. 93%) with a slight enhancement in the case of K⁺, Zn²⁺ and Mg²⁺ ions. The quenching behavior of 23 towards Ni²⁺ was ascribed to the strong interaction of the Ni²⁺ ion with uncoordinated nitrogen and oxygen atoms accessible in the MOF. The K_{sv} value for Ni²⁺ was reported to be 98 127 M⁻¹ with a detection limit of 0.46 μM. This probe was also found to be sensitive to PO₄³⁻ ions but with a relatively higher detection limit (approx. 6.5 μM) compared to Ni²⁺ ions.

During the same period, Peng *et al.*¹⁵² reported Eu³⁺-based MOF 24 bearing 1,2,4-benzene tricarboxylic acid, which acted as an antenna in the MOF. Probe 24 was prepared by the co-precipitation method, and its morphology could easily be adjusted from spherical to irregular honeycomb by simply changing the pH of the reaction medium. The characteristic emission bands of Eu³⁺ were observed near 591 nm, 617 nm and 702 nm due to the typical ⁵D₀ → ⁷F₁, ⁵D₀ → ⁷F₂, and ⁵D₀ → ⁷F₄ transitions, respectively ($\lambda_{ex} = 395$ nm). The sensing ability of 24 was tested against Al³⁺, Zn²⁺, Na⁺, Ca²⁺, Sr²⁺, Ba²⁺, Mg²⁺, Ni²⁺, Cr³⁺, Cu²⁺ and Fe³⁺ ions. Among them, only Fe³⁺, Cr³⁺ and Ni²⁺ displayed considerable luminescence quenching, while no changes could be observed in the case of other metal ions. The luminescence quenching response in 24 was attributed to the 'ion-fence' effect, in which the target metal ion creates a fence surrounding the probe, ultimately interrupting the ligand-sensitized 'antenna effect'.

In the following year (2021), Guan and group¹⁵³ reported Al³⁺-based MOF 25 incorporated with Eu³⁺ and 3,3'-diethyl-oxocarbocyanine iodide (or DOC) organic dye (Fig. 16(a)). This probe had three active luminescent centres, *i.e.*, parent Al³⁺-MOF, Eu³⁺ and DOC, and tuneable luminescence behavior could be realized by systematically adjusting the content of either Eu³⁺ or DOC in the parent MOF. The characteristic Eu³⁺ bands were observed at 578 nm, 592 nm, 614 nm, 652 nm and 688 nm (due to ⁵D₀ → ⁷F_J transitions, where $J = 0-4$) when excited at 350 nm, respectively. The energy transfer efficiency from the ligand to Eu³⁺ could also be tuned by choosing a suitable excitation wavelength. For instance, upon excitation at 360 nm, the intense emission bands for Eu³⁺ and DOC and the organic ligand appeared near 614 nm, 520 nm and 420 nm, respectively (Fig. 16(b)). The luminescence sensor array, hence obtained, could identify Ag⁺, Co²⁺, Cu²⁺, Fe³⁺ and Ni²⁺ by exhibiting variable luminescence quenching in the above-mentioned bands in aqueous medium (Fig. 16(c)).

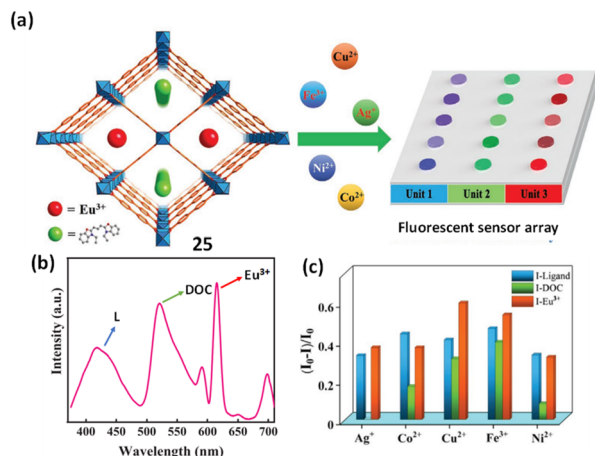


Fig. 16 (a) Construction of the MOF 25-based sensor array; (b) emission spectrum of probe 25 and (c) luminescence response $[(I_0 - I)/I_0]$ of three emitting centers in 25 toward Ag^+ , Co^{2+} , Cu^{2+} , Fe^{3+} and Ni^{2+} ions. Adapted with permission from ref. 153. Copyright 2021, Wiley.

Moreover, LDA (linear discriminant analysis) was employed to differentiate between Ni^{2+} and Co^{2+} , which possess similar behaviour and size with a 5.33% misjudgement in 75 investigated samples. For potential future applications, the metal ion sensing ability of 25 was explored using lake water samples (West Lake), and the discrimination accuracy for individual metal ions (*ca.* 60 μM) was nearly 100%.

In the same year (2021), Perumal and co-workers⁴⁹ employed an interesting strategy for the selective sensing of multiple metal ions. Luminescent nickel-cobalt based MOF 26 equipped with MoS_2 (molybdenum disulfide) nano-box was developed as a biosensor to fabricate a Y-shaped DNAzyme for the multiple-detection of Ni^{2+} , Hg^{2+} and Ag^+ ions in real water samples (Fig. 17(a)). The DNAzyme produced three emission

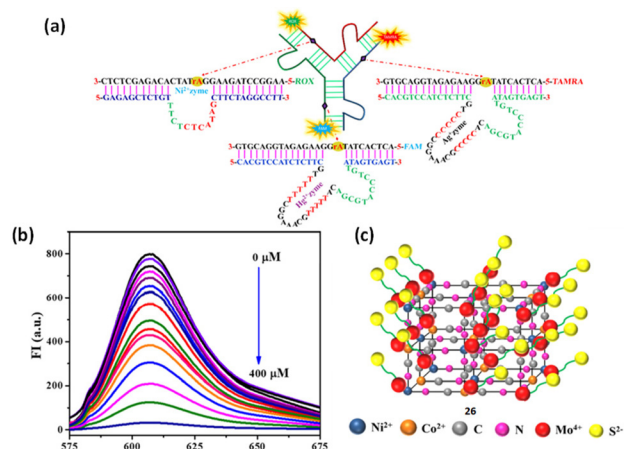


Fig. 17 (a) Structure of Y-shaped DNAzyme labeled with three fluorophores FAM, ROX and TAMRA; (b) fluorescent quenching in the emission band of 26 after the addition of 400 μM Ni^{2+} ions and (c) structure of probe 26. Adapted with permission from ref. 49. Copyright 2021, American Chemical Society.

peaks centred at 523 nm, 606 nm and 572 nm in the absence of the target metal ions. The DNAzyme, labelled with three fluorophores FAM, ROX and TAMRA, displayed a weak binding affinity to the MOF. These fluorophores, acting as substrate aptamers, were cleaved by the interaction between the respective metal ion and the three enzyme aptamers. Therefore, the cleaved substrate aptamers were adsorbed on the surface of the MOF, which exhibited a turn-off response with the help of van der Waals or π - π stacking interactions. Hg^{2+} ions cleaved the aptamer FAM and coordinated with the thymine base pairs, whereas Ag^+ cleaved TAMRA to coordinate with the cytosine base pairs. The alteration of the RNA sites to carbonyl and imidazole functionalities assisted the detection of Ni^{2+} ions with the concomitant release of the ROX substrate aptamer. The response time of probe 26 was 5.0 min with an optimum pH of 8.0. The sensing of Ag^+ , Ni^{2+} , and Hg^{2+} was not affected by the presence of other metal ions such as Zn^{2+} , Co^{2+} , Mg^{2+} , Pb^{2+} , K^+ , Cd^{2+} , Cu^{2+} , Ba^{2+} , Fe^{3+} , Mn^{2+} , Cr^{3+} , Ca^{2+} and Cr^{6+} . The LoD values for Hg^{2+} , Ni^{2+} and Ag^+ ions were calculated to be 0.11, 7.8 and 0.25 nM, respectively. Probe 26 was also able to detect metal ions in spiked lake and tap water samples with an excellent recovery value in the range of 99–103.5%. Initially, the pH of the samples was adjusted to 8.0 using 10 mM Tris-HCl buffer and the diluted samples were spiked with Ni^{2+} ions. The detection results were also reproducible with an RSD value of 3.4%. A similar set of experiments was also performed for Ag^+ and Hg^{2+} ions, suggesting the potential utility of 26 in environmental cation monitoring applications.

Recently, Kabak *et al.* synthesized an Eu^{3+} -based MOF 27¹⁵⁴ using the solvothermal method with 1,4-benzenedicarboxylic acid, 1,10-phenanthroline, and *N,N'*-dimethylformamide as binding units. When excited at 254 nm, 27 exhibited its characteristic emission band at 615 nm due to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. The luminescence of 27 was quenched with Cu^{2+} , Ni^{2+} , and T3, T4 species, while metal ions such as Al^{3+} , Mn^{2+} , Cr^{3+} , Mg^{2+} , Pb^{2+} , Ca^{2+} , Hg^{2+} , Na^+ , Fe^{3+} and K^+ showed negligible changes in water. The Stern-Volmer quenching constant was reported to be $3.19 \times 10^7 \text{ M}^{-1}$ with an LoD of 1.47 μM . This probe was found to be capable of detecting Ni^{2+} ions in drinking and tap water samples in the μM range. The recovery range of 27 (94–102.3%) clearly indicated that this probe can find future application in both *in vitro* and *in vivo* studies.

Mei and Yan (2023)¹⁵⁵ developed probe 28, a zeolitic imidazole framework including 4-aminobenzoic acid, Eu^{3+} ions, and flumequine for the detection of cations in different water sources (such as deionized water, drinking water and nuclear wastewater). The emission spectrum of 28 revealed five emission bands at 578 nm, 596 nm, 616 nm, 652 nm and 700 nm (due to $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions; $J = 0-4$) when excited at 348 nm, respectively. The flumequine is essential to sensitize Eu^{3+} due to the fact that its T1 level (19230 cm^{-1}) is close to that of Eu^{3+} (17500 cm^{-1}), which facilitates efficient energy transfer. Among the investigated metal ions such as Na^+ , K^+ , Li^+ , Ag^+ , Mg^{2+} , Ca^{2+} , Zn^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Hg^{2+} , Mn^{2+} , Ln^{3+} , Ni^{2+} , Cu^{2+} and UO_2^{2+} , probe 28 exhibited quenching with Ni^{2+} , Cu^{2+} , and UO_2^{2+} ions. Furthermore, the addition of NaHCO_3 resulted in

the reappearance of the fluorescence band at 616 nm for UO_2^{2+} ; however, no change was reported in the case of Ni^{2+} and Cu^{2+} . The LoD values for Ni^{2+} , Cu^{2+} , and UO_2^{2+} were reported to be 1.3×10^{-2} , 6.1×10^{-4} , and 9×10^{-3} ppm, respectively. The sensing ability of **28** for Ni^{2+} was also assessed in real drinking water (Tongji University). The addition of Ni^{2+} resulted in the quenching of its emission band; however, the sensitivity in drinking water was lower (2.8×10^{-2} ppm) in comparison to deionized water. Nonetheless, **28** still exhibited a lower LoD than the concentration defined by the EPA. The sensing mechanism was investigated by luminescent lifetime studies, where it was seen that the luminescent lifetime decreased in the case of Ni^{2+} and Cu^{2+} ions; however, the lifetime was not affected in the presence UO_2^{2+} ions. This result suggested that Ni^{2+} and Cu^{2+} follow dynamic quenching, whereas UO_2^{2+} exhibits static quenching. Moreover, the absorption band of UO_2^{2+} overlapped with the excitation spectra of the probe, which supported competitive absorption between the probe and the analyte. The DFT studies revealed that the binding of Ni^{2+} and Cu^{2+} has a large binding energy and chelation causes electron transfer to the metal ion, which suggested PET as the possible mechanism.

5.2 Chromofluorogenic Ni^{2+} sensors

In 2015, Nd^{3+} -based luminescent MOF **29** having bis-dithiocarbamate as an organic linker was synthesized by Xu *et al.*¹⁵⁶ for the chromofluorogenic recognition of Ni^{2+} ions. Probe **29** was found to be stable in methanol but relatively less stable in aqueous media. Three sharp emission bands could be observed in the NIR region at 903 nm, 1077 nm and 1364 nm due to the Nd^{3+} -centred transitions, *i.e.*, ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$, ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ and ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{13/2}$, respectively. The 1D channel and architectural stability of **29** led the authors to assess its ion exchange behavior. The cation exchange experiment was studied *via* 10 min immersion of fresh crystals of **29** in a methanolic solution containing the target metal ions. The crystal structure of **29** was stable only with Ni^{2+} , whereas in the presence of other cations the crystals collapsed. The emission intensity of the band at 1077 nm significantly decreased upon the gradual addition of Ni^{2+} , and the latter was coupled with a change in color of the crystal from light grey to olive (Fig. 18(d)). The quenching constant was computed to be 84.89 M^{-1} , and the quenching mechanism was ascribed to a combination of dynamic and static quenching processes. The authors suggested that the dynamic quenching may be governed by the collisions existing between the ligand and Ni^{2+} , while simultaneously the static quenching mechanism may occur due to the interactions existing between the S groups of the ligand and the Ni^{2+} ion.

In 2017, Sun's group¹⁵⁷ synthesized heterobimetallic MOF (4d–4f species) **30** containing 4-(4-pyridinyl)-benzoic acid and 2-methyl-1*H*-4,5-imidazole-dicarboxylic acid as organic linkers (Fig. 19(a)). The 4f element employed to construct the MOF was Eu, whereas Cd metal was chosen from the 4d series. Probe **30** displayed an excellent luminescent property, and therefore employed for the detection of different metal ions.

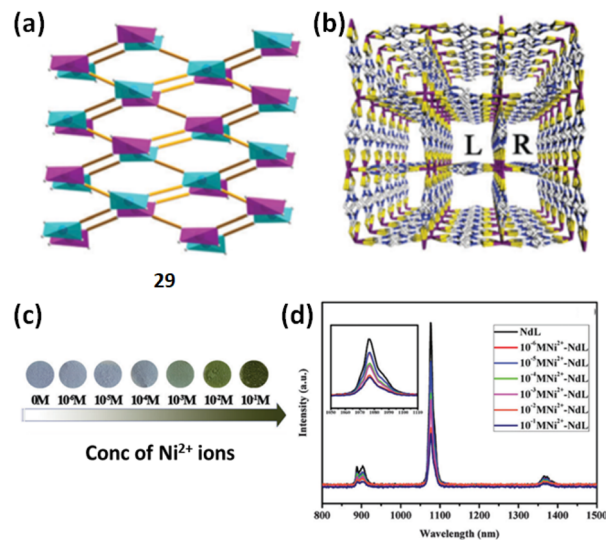


Fig. 18 (a) Interpretation of 1d channel of Nd-based MOF **29**. (b) Channel enclosed by R-helices and L-helices. (c) Probe **29** after immersion in Ni^{2+} solution and (d) changes in its emission spectrum in the presence of different Ni^{2+} concentrations. Adapted with permission from ref. 156. Copyright 2015, The Royal Society of Chemistry.

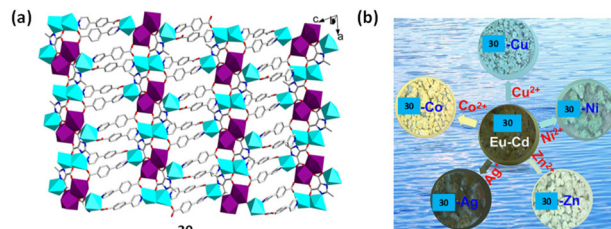


Fig. 19 (a) 2D polyhedral view of probe **30** (colors: Eu = purple, Cd = cyan, O = red, N = blue, and C = gray) and (b) crystal photograph of **30** dispersed in aqueous metal solution. Adapted with permission from ref. 157. Copyright 2017, American Chemical Society.

The emission spectrum of **30** displayed three characteristic bands at 592 nm, 617 nm and 686 nm, typically due to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transitions, respectively. The emission decay lifetime of this MOF was 673 μs , which was fitted by a double-exponential curve. Owing to the presence of carboxylic groups, the luminescence response of **30** was tested against many cations, organic solvents, and organic amine molecules. The powdered MOF was immersed in 0.1 M aqueous solutions of K^+ , Er^{3+} , Li^+ , Na^+ , Ca^{2+} , Ag^+ , Mg^{2+} , Zn^{2+} , Cd^{2+} , Ba^{2+} , Pb^{2+} , Al^{3+} , Cu^{2+} , Co^{2+} , Cr^{3+} , Fe^{3+} and Ni^{2+} to monitor the changes observed in the emission spectrum of **30**. The Mg^{2+} ion caused a significant enhancement in the luminescence intensity of **30**. Alternatively, an emission quenching response was observed in the case of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Ag^+ ions. The probe was sensitive to the metal ions in the order of $\text{Cu}^{2+} > \text{Ag}^+ \approx \text{Co}^{2+} \approx \text{Ni}^{2+} \approx \text{Zn}^{2+}$. The color change to blue, green, light yellow, dark brown and yellow was obvious, respectively, for Cu^{2+} , Ni^{2+} , Zn^{2+} , Ag^+ and Co^{2+} ions (Fig. 19(b)).

The PXRD patterns for the probe and the probe-cation adduct were similar, which confirmed the stability of the framework. The cations concurrently competed when the probe was excited, which resulted in the luminescence quenching. The interaction between the uncoordinated carboxylate and target ion altered the energy of singlet- and triplet- excited states, leading to the inhibition of the 'antenna effect' with a simultaneous reduction in the energy transfer from the ligand to the Eu(III) ion.

6. Conclusions

The present review highlighted the optical detection of Ni²⁺ using metal complexes and MOFs as receptors. Although this review covered the detection of only Ni²⁺, a total of 30 metal-organic probes was discussed, signifying the importance of this research field. As observed from the summarized examples, the luminescent/colorimetric sensing of nickel ions substantially relies on the binding-based approach, while interacting with metal complexes and/or MOFs. The extent of the interaction between nickel ion and the binding unit depends on both the nature of the target ion, *i.e.*, Ni(II), and the donor groups incorporated in the receptor. Therefore, the significance of Pearson's HSAB (hard and soft acid and base) principle emphasizing the role of different donor atoms has been consistently highlighted, which is a key feature for a highly selective and sensitive detection process.

Beyond their advantageous design flexibility and their conspicuous properties (notably compared to their organic counterparts), the consideration of metal complexes as receptors also implies several distinct mechanisms to propitiously design luminescent and colorimetric molecular probes. Among these rationales, PeT is recurrently reported as the typical mechanism for cation-responsive luminescent probes, while the intramolecular charge transfer (*i.e.*, ICT) process is usually assessed for colorimetric probes. However, despite their significance in sensing, it has been realized that several metal complexes display a lack of selectivity for the detection of Ni²⁺ in presence of Cu²⁺. These observations further cement the vital aspect of the judicious choice of donor groups in receptors to achieve the highly selective sensing of a specific metal ion.

In case of MOFs, the presence of N- and O-containing groups was found to be very important for the detection of Ni²⁺ ions; however, Co²⁺ acts as the major interfering species due to its competitive ionic radius and borderline acid character similar to that Ni²⁺. However, despite the significant research devoted to cation-responsive MOF-based probes, their successful industrial implementation is still limited. This is attributed to the insufficient or missing stability/solubility of several MOFs in pure water. Therefore, the development of water-stable MOF receptors remains in high demand in modern research. In many cases, poor water solubility and mechanical strength are recurring disadvantages of MOFs, restraining their practical applications in various research fields. The water solubility of MOFs can also be improved by

employing suitable linker groups such as triazolates, imidazolates and tetrazolates in the ligand framework.^{158,159} Recently, the development of magnetic MOF (MMOF) composites has been attracting increasing attention from researchers in the sensing field due to their easy separation and reusability features.¹³⁰

Also, near-*infra*-red (NIR)-active probes (optical window: 690–900 nm) should be emphasized. Alternatively, with respect to sustainability, the relative complexity of some sensing materials coupled with their unsatisfactory synthesis (*e.g.*, low yields, tedious synthesis or purification steps, and high costs) may harm the environment, humans and living beings in general. Therefore, with the support of green chemistry, environment-friendly synthetic strategies are urgently required to be adopted for future sensing materials. An alternative way is to design and develop recyclable and degradable sensors, which may help reduce environmental pollution on a large scale.^{160,161} We hope that the significant collection of Ni²⁺ sensing probes compiled in this review will help build further comparative systematic SAR screenings and mechanistic investigations for the design of competitive sensors, which is the imperative first step before considering subsequent adequate solutions or treatments to the drawbacks of their overuse/mishandling.

Data availability

Data are available on request from the authors.

Conflicts of interest

There are no conflicts to declare.

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