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Rhodamine-Derived Fluorescent Sensors for Selective Detection of Pb(II): Present Developments and Future Outlooks – A Focused Short Review

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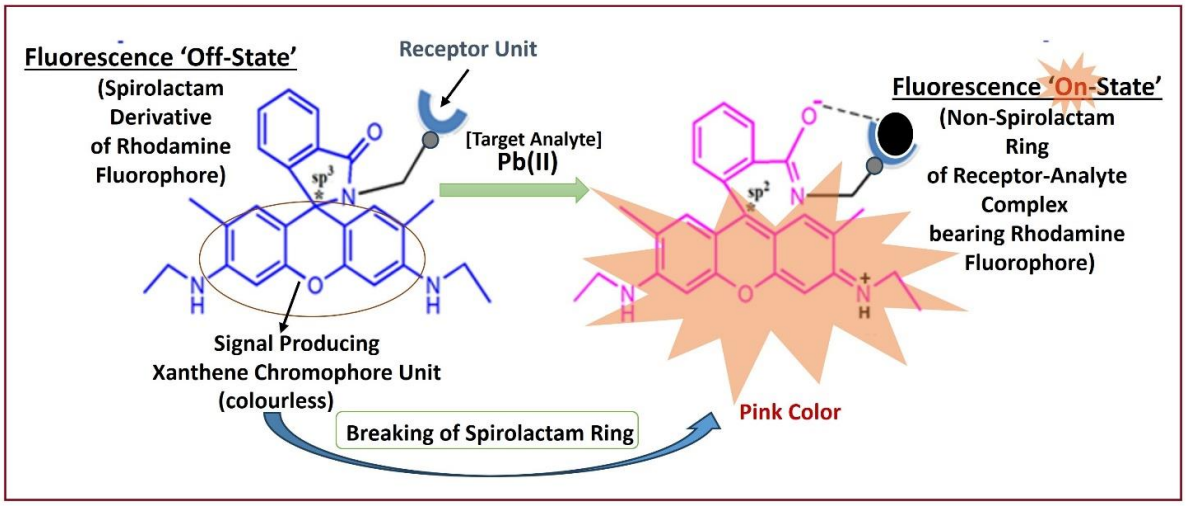
ABSTRACT

This focused short review highlights recent progress in rhodamine-derived fluorescent sensors designed for the selective detection of toxic Pb(II) ions. These sensors primarily operate through a spirolactam ring-opening mechanism, which produces a distinct fluorescence signal upon binding with Pb(II), enabling sensitive and selective detection. The review emphasizes various structural modifications of the rhodamine framework that have significantly enhanced sensor performance, including improved sensitivity, higher selectivity against competing metal ions, and better practical applicability. Such refinements have paved the way for real-world uses, particularly in environmental monitoring of lead contamination and biomedical diagnostics. Looking ahead, future research aims to address challenges related to sensor stability and robustness to ensure consistent performance over time. Additionally, there is a growing interest in developing multiplex sensing capabilities to detect multiple analytes simultaneously, broadening the utility of these sensors. Integration with portable and user-friendly devices is also a key focus, which would enable rapid, on-site Pb(II) detection without the need for sophisticated laboratory equipment. Together, these advancements hold promise for making Pb(II) detection more accessible, efficient, and versatile, contributing significantly to public health and environmental safety efforts worldwide.



Schematic presentation of the change of cyclic-lactam form to an acyclic-xanthene form of Rhodamine derivative on binding to Pb(II) (Target Analyte)

Keywords: Rhodamine, Pb^{2+} detection, Fluorescent chemosensor and chemodosimeter, FRET.

INTRODUCTION

With the rapid growth of global industrial activities, environmental pollution—especially water contamination—has become a critical concern worldwide. Among various pollutants, heavy metal ions are particularly dangerous due to

their persistence in ecosystems, potential to bioaccumulate, and high biological toxicity even at trace levels. Lead (II) ions (Pb^{2+}), a common heavy metal contaminant, disrupt cellular metabolism by inhibiting sulfhydryl-containing enzymes and binding to amino and amide groups. This disruption can cause serious health issues such as immunosuppression, neurological disorders, and cancer. Therefore, accurate and timely detection of Pb^{2+} in environmental, agricultural, and food samples is vital to protect public health.[1]

Despite the availability of conventional detection methods like inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS), and surface-enhanced Raman spectroscopy (SERS), their reliance on costly instrumentation and complex sample preparation limits their applicability for rapid and onsite monitoring. Consequently, there is an urgent need for simple, rapid, sensitive, and selective detection approaches that can be deployed easily in the field.

In response to this challenge, fluorescence-based detection methods such as chemosensors and chemodosimeters have emerged as promising alternatives. Chemosensors typically provide reversible and selective binding interactions with Pb^{2+}, producing immediate and real-time fluorescent or colorimetric responses. In contrast, chemodosimeters operate via irreversible chemical reactions upon interacting with Pb^{2+}, offering high selectivity by inducing permanent changes in the sensor molecule. Both strategies enable sensitive detection with distinct advantages, broadening the toolkit for environmental monitoring.

This review focuses on recent advances in rhodamine-based fluorescent sensors for Pb^{2+} detection. Rhodamine derivatives exhibit unique spirocyclic structures that undergo a fluorescence "off–on" transformation upon interaction with Pb^{2+}, providing distinct colorimetric and fluorometric signals. Their tunable structures, excellent fluorescence stability, and biocompatibility make them ideal candidates for developing effective Pb^{2+} sensors.[2-4]

Here, we summarize the current strategies and mechanisms behind rhodamine-based Pb^{2+} sensing, discuss their advantages and limitations, and explore future perspectives including integration with portable devices and paper-based platforms. By providing a comprehensive overview, this review aims to facilitate the development of more robust, cost-effective, and field-deployable Pb^{2+} sensors to support environmental monitoring and safeguard public health worldwide.

Design Strategies for Rhodamine-Based Pb(II) Sensors:

This review systematically examines rhodamine-based fluorescent chemosensors for the selective detection of Pb(II), focusing on recent advances in rhodamine derivatives. It highlights their structural diversity, sensitivity, selectivity, and practical applications. Rhodamine sensors typically operate via a spirolactam ring-opening mechanism. In the absence of metal ions, they remain colorless and non-fluorescent. Binding to target metal ions triggers spirolactam ring opening, causing a pink color and strong fluorescence, which enables both sensitive detection and visible color change.

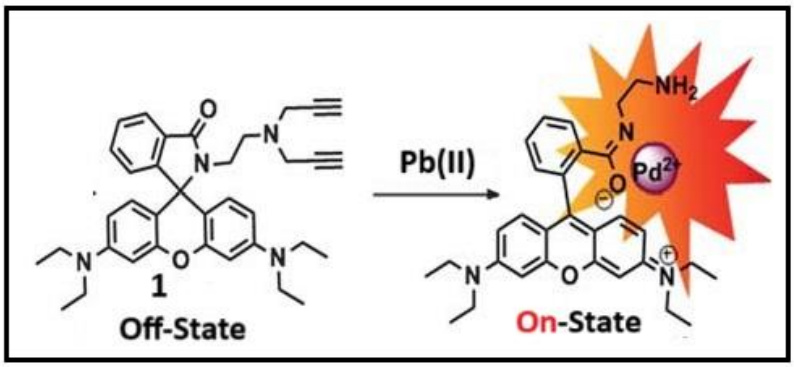


Fig. 1: Structure of Rhodamine-based chemodosimeter (1) for Pb^{2+}.

Liu et al. synthesized a bis-propargyl rhodamine B chemodosimeter (1) (Fig. 1) that exhibits a 113-fold fluorescence increase upon binding with Pd^{2+}, demonstrating high selectivity over other metal ions. The Pd^{2+}-catalyzed depropargylation triggers a "turn-on" fluorescence response via spirolactam ring opening, as confirmed by FTIR and NMR analyses. The chemodosimeter also detects Pd^0 without the need for a reducing agent, showing similar emission intensity and a faster response in the presence of PPh_3. Compared to its cyclohexane analogue, the rhodamine unit enhances fluorescence by 500-fold. Fluorescence imaging with receptor (1) highlights its potential for Pd^{2+} detection in living cells.[3]

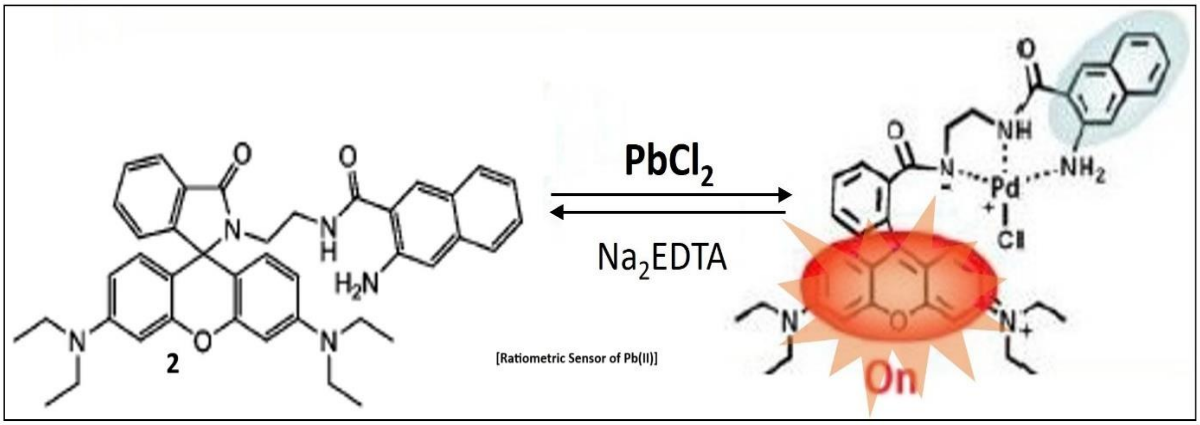


Fig. 2: Structure of Rhodamine-based Ratiometric chemosensor (2) for Pb^{2+}.

Peng et al. designed and synthesized a naphthylamine–rhodamine hybrid ratiometric and colorimetric fluorescent 'Off-on-Off' chemosensor (2) (Fig. 2) with high selectivity and sensitivity for detecting Pd^{2+} ions. Additionally, this probe demonstrated the capability to monitor Pd^{2+} ions in live mice through fluorescence imaging.[4]

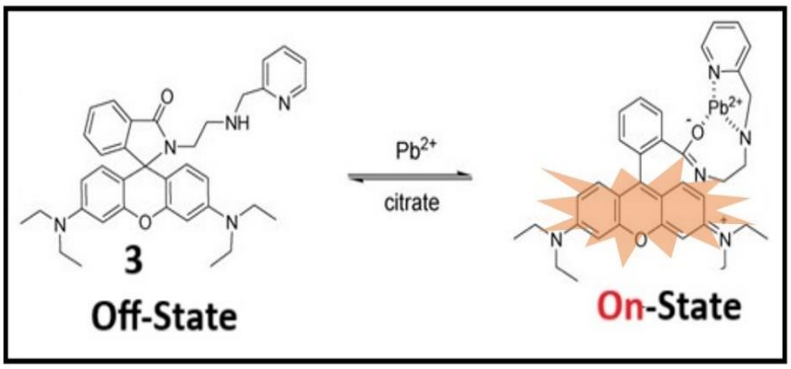


Fig. 3: Structure of Rhodamine-based chemosensor (3) for Pb^{2+}.

C-Y Li et al. developed a novel rhodamine-based fluorescent chemosensor (3) for colorimetric and fluorescent detection of citrate in aqueous solution—the first of its kind. The sensor shows Pb^{2+}-induced fluorescence quenched by citrate, enabling detection via color and fluorescence changes at long wavelengths. It responds linearly to citrate from 1.0×10^{-7} to 5.0×10^{-5} M with a 2.5×10^{-8} M detection limit, is fast (<1 min), pH-independent (6.0–8.0), highly selective, and successfully applied to urine samples.[5]

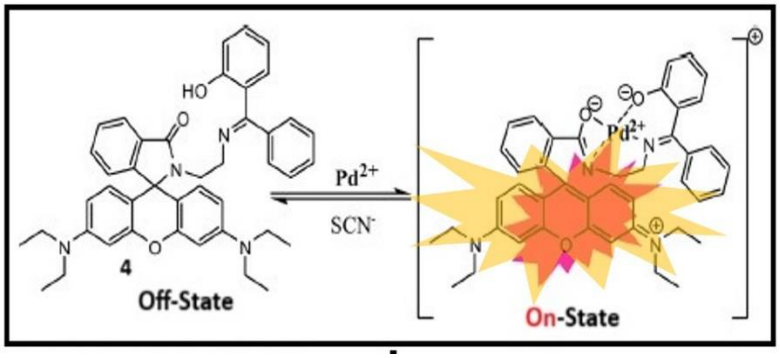


Fig. 4: Structure of Rhodamine-based chemosensor (4) for Pb^{2+}.

Sinha et al. developed a spirolactam-functionalized rhodamine-appended benzophenone (4) (Fig. 4) probe for sensitive and selective fluorogenic detection of Pd^{2+} in aqueous ethanol at pH 7.4. It was characterized by NMR, ESI-MS, FT-IR, and X-ray diffraction. It showed a low detection limit of 34 nM, below WHO safety levels. The sensing involved a 1:1 complex with Pd^{2+}, confirmed by multiple analyses and computational studies explaining fluorescence enhancement via spirolactam ring opening. The probe was successfully used for Pd^{2+} imaging in MDA-MB-231 cells.[6]

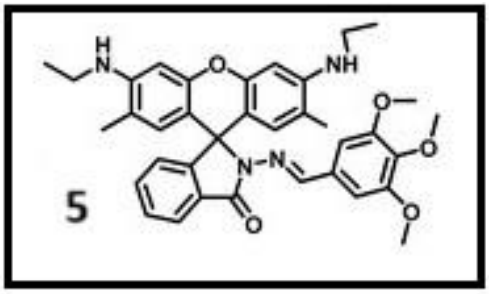


Fig. 5: Structure of Rhodamine-based chemosensor (5) for Pb^{2+}.

Sivaraman et al. designed and synthesized a rhodamine-based derivative (5) (Fig. 5) as a highly sensitive and selective chemosensor for Pb^{2+} ions. The probe detected Pb^{2+} at nanomolar concentrations (15 nM). DFT calculations revealed that the photophysical changes arose from internal charge transfer alterations followed by spirolactam ring opening. Additionally, it successfully detected Pb^{2+} in HeLa cells under physiological conditions.[7]

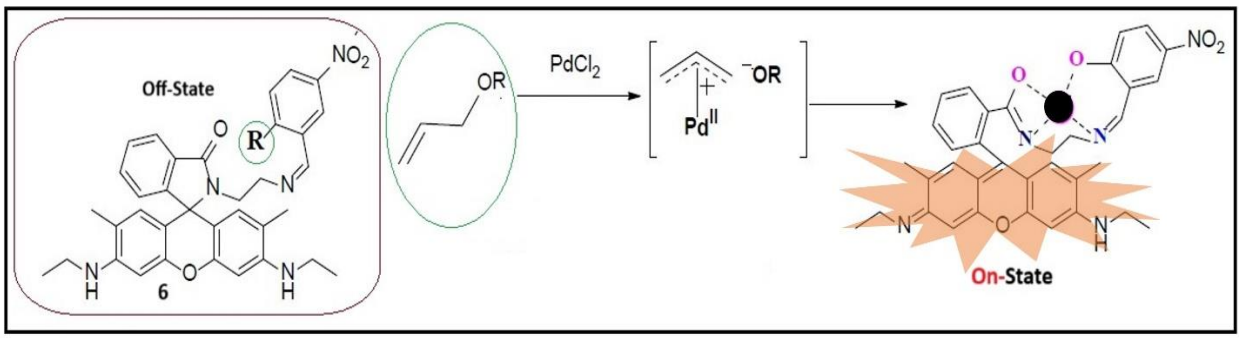


Fig. 6: Structure of Rhodamine-based chemodosimeter (6) for Pb^{2+}.

Sinha et al. reported a rhodamine-appended allylic iminephenol (6) (Fig. 6) served as a 'turn-on' fluorescent chemosimeter for Pd^{2+} with a detection limit as low as 50 nM. Mechanistic studies showed that Pd(II) triggered terminal (C–O)-allyl cleavage followed by spirolactam ring opening, causing significant changes in fluorescence intensity and energy. The fluorescence sensing was applied for imaging Pd^{2+} species in living cells under physiological conditions.[8]

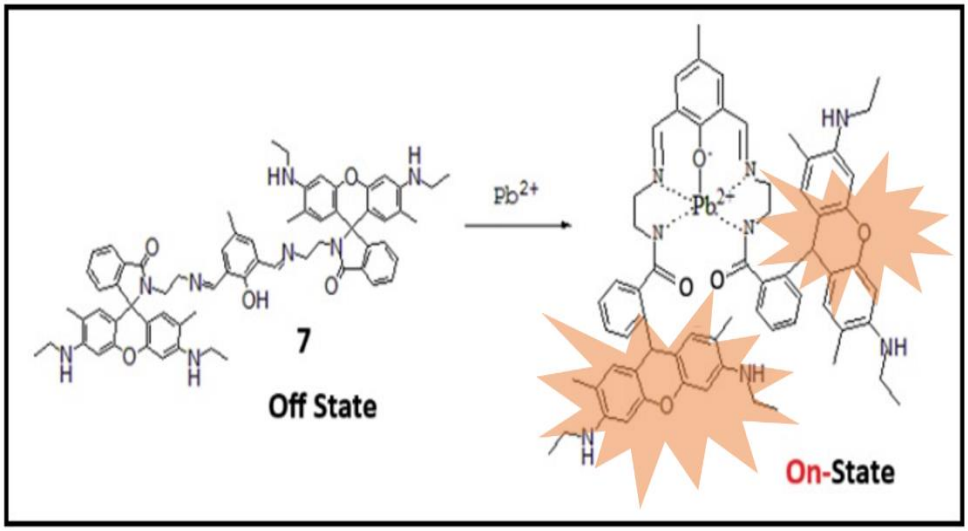


Fig. 7: Structure of Rhodamine-based chemosensor (7) for Pb^{2+}.

Niu et al. reported a new rhodamine derivative (7) (Fig. 7) as a selective and sensitive fluorescent chemosensor for Pb^{2+} in aqueous solution. It enabled visual detection by changing color from light yellow to pink. The fluorescence response was triggered by Pb^{2+}-induced ring-opening of the spirolactam (non-fluorescent) to acyclic-xanthene (fluorescent). It showed a 1:1 binding ratio with a linear detection range of 1.0×10^{-8} to 1.0×10^{-5} M and a detection limit of 2.7×10^{-9} M.[9]

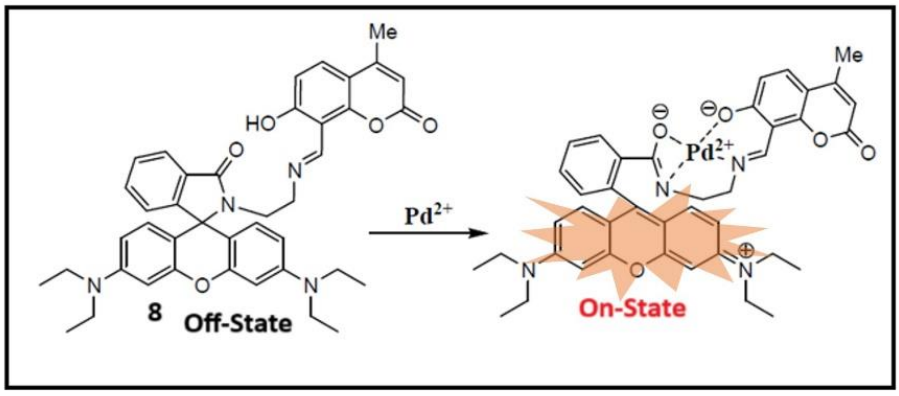


Fig. 8: Structure of Rhodamine-based chemosensor (8) for Pb^{2+}.

Sinha et al. reported that coumarinyl-rhodamine (8) (Fig. 8) acted as a highly selective sensor for Pd^{2+} in ethanol/H_2O (8:2) with a detection limit of 18.8 nM. It was weakly emissive alone but showed strong pink fluorescence at 598 nm upon Pd^{2+} binding. The sensing involved spirolactam ring opening confirmed by DFT studies. It formed a 1:1 complex with Pd^{2+} ($Ka = 9.1 \times 10^4\ M^{-1}$), validated by Job's plot, mass spectra, and Benesi–Hildebrand analysis. It also selectively detected Pd^{2+} in MCF7 cells in vitro.[10]

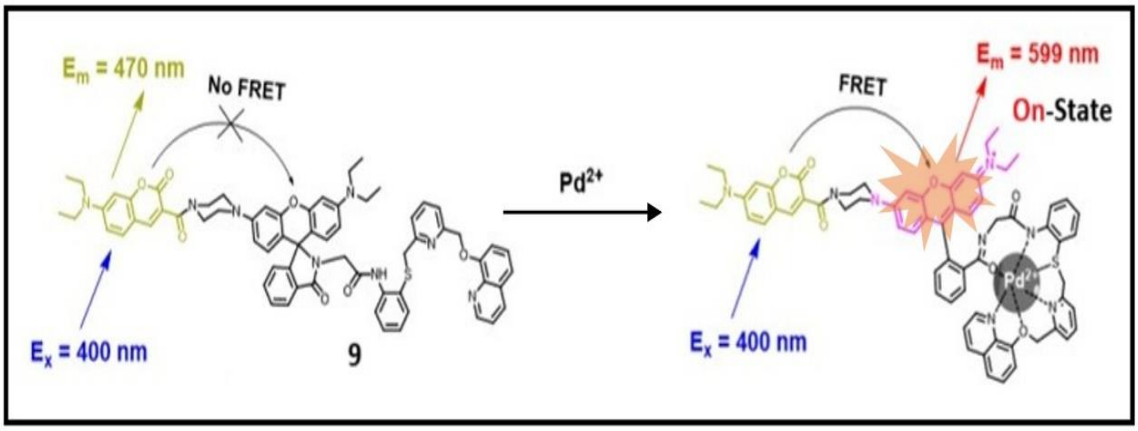


Fig. 9: Structure of Rhodamine-based chemosensor (9) for Pb^{2+}.

A rhodamine-based palladium coumarin-rhodamine Förster resonance energy transfer (FRET)-pair based palladium sensor was synthesized with the designed podand ligand for Pd^{2+} ion recognition. It showed both colorimetric and fluorometric changes in the presence of Pd^{2+} ion due to the opening of its spirolactam rings. It exhibited low cell cytotoxicity and was successfully used to image Pd^{2+} in BEAS-2B lung epithelial cells.[11]

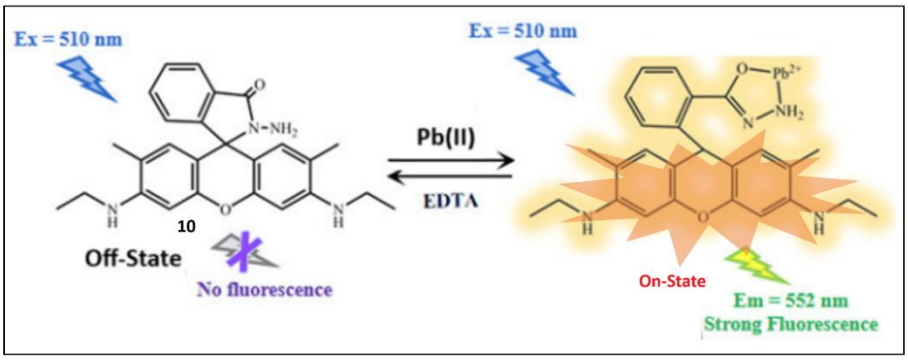


Fig. 10: Structure of Rhodamine-based chemosensor (10) for Pb^{2+}.

Wang et al. synthesized rhodamine 6G hydrazide (10) (Fig. 10) as an 'off–on' dual-mode fluorescence and visual sensor for Pb^{2+}, which exhibited strong fluorescence stability and reversibility. Under optimized conditions, the sensor detected Pb^{2+} in the range of 0.05 to 6.0 μM ($R^2 = 0.9851$) with a detection limit of 0.02 μM. In spiked agricultural and

food samples, recovery rates ranged from 84.0% to 102.0% (RSD < 5%), showing good correlation with ICP-MS data ($R^2 = 0.9915$).[12]

CONCLUSION AND FUTURE OUTLOOKS

In conclusion, rhodamine-based "turn-on" fluorescent sensors offer a straightforward, rapid, and visually detectable approach for selective Pb^{2+} detection, particularly in aqueous environments. Their demonstrated effectiveness in environmental and food sample analysis underscores their potential for real-time monitoring. Looking ahead, future developments aimed at improving sensitivity, selectivity, stability, and device integration will likely expand their practical applications, enabling more widespread and portable heavy metal detection solutions.

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