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visualization of plant health and their living environment in sustainable agriculture

Fluorescent chemosensors facilitate the

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Globally, 91% of plant production encounters diverse environmental stresses that adversely affect their growth, leading to severe yield losses of 50-60%. In this case, monitoring the connection between the environment and plant health can balance population demands with environmental protection and resource distribution. Fluorescent chemosensors have shown great progress in monitoring the health and environment of plants due to their high sensitivity and biocompatibility. However, to date, no comprehensive analysis and systematic summary of fluorescent chemosensors used in monitoring the correlation between plant health and their environment have been reported. Thus, herein, we summarize the current fluorescent chemosensors ranging from their design strategies to applications in monitoring plant-environment interaction processes. First, we highlight the types of fluorescent chemosensors with design strategies to resolve the bottlenecks encountered in monitoring the health and living environment of plants. In addition, the applications of fluorescent small-molecule, nano and supramolecular chemosensors in the visualization of the health and living environment of plants are discussed. Finally, the major challenges and perspectives in this field are presented. This work will provide guidance for the design of efficient fluorescent chemosensors to monitor plant health, and then promote sustainable agricultural development.

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1. Introduction

Exploring and understanding plant-environment interactions are essential components of sustainable agriculture, which is crucial for ensuring crop production and food security. Reportedly, global food production has increased by over threefold due to the advancement in sustainable agricultural practices regarding the connection between plant health and their environment during the past 50 years. Balancing the relationship between plants and their environment to regulate plant health can increase grain production by 33 million tons and decrease nitrogen fertilizer utilization (1.2 million tons), which is equivalent to an enhanced net worth of \$12.2 billion.² Plant health is directly associated with biodiversity, plant productivity, soil conditions, water quality, and climate change, thereby facilitating

the health and living environment of plants. Traditional methods including molecular technology and chromatographic detection are regularly employed. For example, DNA amplification via polymerase chain reaction (PCR) and its derivatives, namely nested PCR, quantitative PCR, digital PCR, and multiplex PCR, enzyme-linked immunosorbent assay (ELISA), and loop-mediated isothermal amplification (LAMP) are scientific testing methods for plant diseases.^{5,6} Also, ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/ MS), gas chromatography-mass spectrometry (GC-MS), high performance liquid chromatography (HPLC) and other chromatographs are utilized to identify pesticide residues, soil or water contamination, and fruit nutrition.7-10 However, these

amplified ecosystem services and mitigating the dependence on extrinsic resources.3 For example, soil serves as the primary medium for plants, and consequently the presence of certain pollutants such as heavy metals in the soil may negatively impact both plant growth and human dietary safety.4 Therefore, monitoring the health and living environment of plants in sustainable agriculture is necessary for promoting the development of the economy and society. To date, many technologies have been developed to monitor

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procedures are laborious and time-consuming, often necessitating complex processes and proficient professionals for operation, and they fail to exhibit continuous monitoring. Consequently, due to their advantages of high sensitivity, simple operation, and spatiotemporal resolution, fluorescent chemosensors have gradually matured in exploring the connection between the health and living environment of plants.

In recent years, different types of fluorescent chemosensors including small-molecules and nano and supramolecular complexes have been used for monitoring plant health and their environment. The reasonable design of small-molecule fluorescent chemosensors using diverse chromophores such as naphthalimide, coumarin, BODIPY, rhodamine, and cyanine have been extensively applied for monitoring plant health owing to their low cost and favorable biocompatibility. 11,12 Furthermore, to increase the quantum yield (QY) and recyclability, fluorescent nano-chemosensors have been designed based on quantum dots, metal-organic frameworks, covalent organic frameworks and nanoclusters and used to analyze the

living environment and health of plants. 13-15 The fluorescent supramolecular chemosensors formed polymer and hydrogelator systems could realize recyclability and high-specificity monitoring of the living environment of plants and food security. 16-18 Consequently, fluorescence-based techniques have become one of the sustainable agriculture hotpots for monitoring plant health and their surroundings. Nevertheless, there is a lack of summary and critical reviews establishing the corresponding relationship between fluorescent chemosensors and the major issues in plantenvironment interactions.

Herein, we present a comprehensive analysis on the progression and application of fluorescent chemosensors in monitoring the health and living environment of plants. The commonly used design strategies, mechanisms, and challenges associated with fluorescent chemosensors in monitoring and analyzing plant-environment interactions are introduced. Most importantly, we systematically discuss the application of smallmolecule, nano and supramolecular fluorescent chemosensors in areas such as plant growth and development, abiotic and



Ting Wen, Yang-Yang Gao, Jie He (first row from left to right) Xiao-Hong Li, Hong Wu, Jian-Hong Li (second row from left to right)

There are six authors in the photo including Ting Wen, Yangyang Gao, Jie He (first row from left to right), and Xiaohong Li, Hong Wu, Jianhong Li (second row from left to right). Yangyang Gao received her PhD degree from Shandong Agricultural University with Prof. Feng Liu and Prof. Wei Mu, and subsequently worked with Prof. Gefei Hao as a Postdoctoral Researcher at the State Key Laboratory of Green Pesticide in Guizhou University. She is interested in the areas of the interaction of plants and fungal pathogens and sustainable measures for maintaining plant health. Jie He and Xiaohong Li are currently pursuing a PhD degree at the State Key Laboratory of Green Pesticide in Guizhou University. Their research is focused on using nanotechnology to improve the stress resistance of plants and fluorescent chemosensors, respectively. Jianhong Li, Hong Wu, and Ting Wen are currently pursuing their Master's Degree at State Key Laboratory of Green Pesticide in Guizhou

University. Their research focus is the design and synthesis of fluorescent probes, the design of biosensors based on genetic coding, and the application of imaging techniques for plant health analysis, respectively.



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Jun Li earned his PhD in 2014 from Central China Normal University. Subsequently, joined Prof. Juyoung Yoon's research group at Ewha Womans University as a Postdoctoral Fellow in 2015-2017. He is now an Associate Professor at Huaz-University, hong *Agricultural* P. R. China. His research interest mainly focuses on small-moleculebased fluorescent probes and their applications in plant imaging.



Ge-Fei Hao

Ge-Fei Hao, a Professor at Guizhou University, specializes in pesticide informatics research. Prof. Hao is a recipient of the National Science Fund for Distinguished Young Scholars and a chief scientist leading national key research and development projects. He has also been selected for the Ministry of Education's "Changjiang Scholars Reward Plan" for young scholars. He is focused on the key scientific issue of "the interaction between biomolecules and pesticides" in

pesticide innovation. He established the world's first systematic pesticide informatics platform.

Affecting plant health Plant elements Signaling Cell Metabolites Biotic stresses components molecules ROS; Protein; Phenolic RNS: Nucleic acid Bacteria compounds; RSSs: Polysaccha-Hormones: Alkaloids; Polypeptide; Carotenoids Virus Insects **Nutrition utilization** Abiotic stresses MINERAL Sugar Heavy Pigments Temperature Drought meatal Pectin, Na⁺ Na⁺ Na⁺ Microbial Water Nutrient conditions Salt pollutant deficiency

Fig. 1 Relationship between the health and living environment of plants. Biotic and abiotic stresses and nutrition utilization are major issues affecting plant health, which can reflect the changes in plant contents including signaling molecules (e.g. ROS, RNS, RSSs, hormones, Ca²⁺, and NO), cell components (e.g. proteins, nucleic acids, polysaccharides, polypeptides, and lipids), metabolites (e.g. phenolic compounds, flavins, alkaloids, and carotenoids), metal ions and microenvironment (e.g. pH and pesticides).

Living environment

biotic stresses, soil conditions, irrigation water quality and nutrition utilization. Meanwhile, we correlate the characteristics of chemosensors with their application, and then provide insights into designing efficient and suitable sensors. Lastly, we summarize the network of fluorescent chemosensors to promote the understanding of the connection between plant health and their environment. This work will provide guidance for the future development of efficient fluorescent chemosensors, thereby realizing the real-time monitoring of the health and living environment of plants in sustainable agriculture.



Juyoung Yoon is a distinguished Professor at the Department of Chemistry and Nanoscience, Ewha Womans University. His research interests include investigations of fluorescent chemosensors, activatable photosensitizers, phototherapy and theranostics. He was listed as a highly cited researcher in chemistry since 2014.

Juyoung Yoon

Monitoring plant health and their living environment in sustainable agriculture

2.1 The relationship between plant health and their environment

Plant health not only depends on the inherent potential of plants but also has a close relationship with environmental factors including abiotic and biotic stresses and nutrient utilization (Fig. 1).19 Abiotic and biotic stresses mainly focus on evaluating the relationship between the elements and living environment of plants.20 This is because abiotic (e.g. salinity, drought, temperature, heavy metals, and pesticides) and biotic stresses (e.g. phytoparasitic nematodes, fungi, and bacteria) are the most serious factors affecting plant growth and development. For example, drought and high temperature can cause wilting, leading to reduced photosynthesis, impaired nutrient uptake, protein denaturation, cellular damage, and ultimately plant death. Excessive levels of heavy metals can accumulate in plant tissues, disrupting cellular processes and inhibiting their growth. Biotic stresses can cause physical or tissue damage, nutrient deficiencies, and potentially mortality. During the interaction process of plants and an adverse environment, monitoring the changes in plant elements including signaling molecules (e.g. ROS, RNS, RSSs, hormones, Ca2+, and NO), cell

components (e.g. protein, nucleic acid, polysaccharide, and polypeptide, lipid), metabolites (e.g. phenolic compounds, flavins, alkaloids, and carotenoids), metal ions and microenvironments (e.g. pH and pesticides) can assess plant health, and then timely strategies applied to regulate the plant's response to various environmental stresses. 21,22 The efficiency of nutrient utilization is the determining factor of fruit quality, serving as the pivotal link between plant health and agricultural product supply chains. Nutrient utilization mainly depends on the diversity and equilibrium of beneficial microorganisms, nutrient sources and content, soil characteristics, water conditions, and plant health.²³ Therefore, monitoring the response of plants to abiotic and biotic stresses, their living environment, and nutrition supplication and utilization is essential for understanding the interactions between plants and their environment and promoting plant health in sustainable agriculture.

Currently, an array of techniques including visual assessment, PCR, immunological approaches, biochemical analysis technologies, chromatography and mass spectrometry methods, electrochemical sensors, visible light imaging, imaging spectroscopy, thermal infrared imaging and three-dimensional imaging have been used to monitor plant-environment interactions (Table 1). Visual assessment is a commonly utilized reliable strategy for evaluating plant stress phenotypes, although it has low sensitivity and is time consuming, as well as associated with subjectivity bias due to expert interpretation.²⁴ Alternatively, PCR and immunological techniques can effectively detect plant pathogens within smaller sample sizes, with increased sensitivity and precision, but involve higher testing expenses, intricate procedures, specialized operation, non-living surveillance and potential occurrence of false positives. 25 Biochemical analytical technologies are well-suited for analyzing the delicate, specific and trace analysis of plant health biomarkers in the laboratory, but their inability to conduct real-time detection and complex operation processes necessitate consideration.²⁶ Chromatography coupled with mass spectrometry techniques (e.g. UPLC-MS/ MS, LC-MS and GC-MS) facilitate the precise determination of compound identity, quantification, and separation in complex samples, featuring high sensitivity and rapid analysis, but the required instruments are costly and the detection sensitivity can occasionally be affected by substrate interference.²⁷ Visible light imaging represents another alternative that employs digital images to capture plant phenotype at relatively lower costs, user-friendly operational pattern, and straightforward maintenance requirements, but its image quality can potentially be hindered by background factors and illumination conditions.²⁸ Imaging spectroscopy utilizes the interaction between the solar radiation generated from samples, providing high spatial resolution over a broad spectral range. However, the high cost and the significant data storage demands for multi-spectral and hyperspectral imaging instruments should also be considered.²⁹ Thermal infrared imaging offers simplicity and high-resolution for quantifying the infrared radiation released by samples, though a difficulty is deciphering the infrared radiation released by samples. Meanwhile, deciphering the temperature of soil and

plants beneath sparse canopies under irregular environmental conditions is a persistent challenge.³⁰ Three-dimensional imaging can precisely quantify the electric or laser emission produced by specimens, exhibiting superior spatial resolution and robust resistance to interference, but the employed methodologies impose significant financial burden, necessitate extended scanning durations, and yield modest throughput rates.31 Thus these issues, fluorescence-based technologies can counterbalance the abovementioned disadvantages, which have developed rapidly and now extensively applied in monitoring the health and living environment of plants to promote the development of sustainable agriculture.

2.2 Advantages of fluorescent chemosensors

Compared with the above-mentioned technologies, fluorescencebased technology possesses advantages for visualizing plant health and their environment in some aspects, as follows:32-34 (i) for easy detection, fluorescent chemosensors emit bright and distinct signals, facilitating the detection of the presence and localization of specific components in plants or in their living environment. (ii) For specificity, fluorescent chemosensors can be designed based on the characteristics of specific targets, molecules or compounds of interest. This allows the selective identification and quantification of specific markers for implying plant health. (iii) For real-time monitoring, fluorescent chemosensors facilitate the real-time monitoring of plant health indicators. By labeling specific molecules, changes in their concentration or distribution can be observed over time. (iv) For non-destructive analysis, fluorescent chemosensors can be applied externally or systemically absorbed by plants without causing significant damage. This allows repetitive measurement over time, reducing the necessity for destructive sampling and enabling longitudinal studies. (v) For high sensitivity, fluorescent chemosensors are highly sensitive, which can often detect low concentrations of target molecules. This attribute is particularly advantageous in detecting early signs of plant stresses or nutrient deficiencies. (vi) For multiplexing capability, fluorescent chemosensors can be designed with different emission wavelengths, allowing the simultaneous detection of multiple targets within the same sample and facilitating the evaluation of various aspects of plant health. (vii) In terms of high-throughput screening, fluorescent chemosensors are employed in high-throughput screening tests, enabling the expedited examination of an extensive array of plant samples. Therefore, fluorescent chemosensors have been widely used and progressively matured in the analysis of the correlation between plant health and environment.

The classification of fluorescent chemosensors

Fluorescent chemosensors are capable of monitoring plant health under abiotic and biotic stresses, various conditions of soil and water, and nutrient utilization rate. Currently, three major types of fluorescent chemosensors including small-molecule fluorescent chemosensors, fluorescent nano-chemosensors and fluorescent supramolecular chemosensors have been used in the visualization of plant health and their surroundings. Small-molecule fluorescent chemosensors are commonly used in plant imaging owing to their

 Table 1
 Conventional methods for monitoring plant health and their environment

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Techniques	Principles	Advantages	Disadvantages
Visual assessment	Observing plant health status	Most reliable and accurate	Low sensitivity and timeliness
PCR-based methods	Amplification of one or a few copies of a particular sequence of DNA	Fewer samples, timeliness, high specificity and sensitive	Expensive, complicated steps, professional operation, and false positives
Immunology-based methods	Interaction between antibody and antigen	Timeliness and high specificity	Non-real-time detection, and false positive
Biochemical technologies	Biochemical reaction between biomarkers in samples and reagents	High sensitivity and specificity, and trace analysis	Non-real-time detection, and complex operation processes
Chromatography and mass spectrometry	Separation, identification and quantitative analysis of compounds in complex	Timeliness and high-throughput	High expensive cost, and professional operation
Electrochemical sensing	Monitoring the changes in current or potential of sample	High sensitivity and selectivity, low equipment cost	Lack of competitiveness
Visible light imaging	Using digital images to mimic human perception	Low cost, ease of operation and maintenance	False positive
Imaging spectroscopy	Imaging the solar radiation produced from samples	High spatial resolution and wide spectral range	Expensive, and large volume of data for processing
Thermal infrared imaging	Measuring the emitted infrared radiation from the surface of samples	High spatial resolution, and ease of operation	Influenced by environmental temperature or conditions
Three dimensional imaging	Imaging the electromagnetic or laser radiation produced by samples	High three-dimensional spatial resolution, and strong ant-interference capability	High cost, long scanning times, and low throughput

biocompatibility and high spatial-temporal resolution. Most fluorescent nano-chemosensors have been used to monitor the living environment of plants, which is determined by their properties of recyclability and high sensitivity. Meanwhile, fluorescent supramolecular chemosensors are often used to detect fruit quality and the living environment of plants because of their recyclability, high selectivity and strong adaptability. In the following sections, we summarize and analyze the utility of three types of fluorescent chemosensors in monitoring the health and living environment of plants.

3. Applications of small-molecule fluorescent chemosensors

Small-molecule fluorescent chemosensors are powerful tools for visualizing plant health by changing their luminescence emission in response to specific analytes in plants under abiotic and biotic stresses. A variety of small-molecule fluorescent chemosensors based on different fluorophores such as coumarin, naphthalimide, rhodamine, fluorescein, NBD, BODIPY, Nile bule, and cyanine has been discovered and developed (Fig. 2).35 When the parent structure of the fluorophore is modified, the emission spectrum is usually in the range of 500 to 600 nm. NIR fluorescence (near-infrared, 700-900) exhibits some advantages including deeper tissue penetration to circumvent photo-bleaching and minimal phototoxicity.³⁶ Each fluorophore has unique attributes that should be considered, which determine its suitability as a label for studying plant-environment interactions.

3.1 Coumarin derivatives

Coumarin is a bi-cyclic structure consisting of a phenyl unit encircled by a pyrone ring encompassing a rigid C=C bond, a C=O group and six peripheral C-H sites.³⁷ The parent coumarin molecule displays negligible or minimal fluorescence, whereas numerous coumarin derivatives with various substitutes produce considerable fluorescence in the visible light spectrum (400-500 nm). Accordingly, hundreds of coumarin dyes have been engineered due to their increased fluorescent QY, adaptability of their emission wavelengths and responsiveness to their microenvironmental polarity. Observational research has explored the relationship between the photophysical attributes of coumarin derivatives and their chemical compositions, showing that substitutions on the coumarin fragment result in blue- or red-shifted fluorescence phenomenon.³⁸ In terms of electronic structure, the introduction of electron-withdrawing entities at positions 3 or 4, or electron-donor moieties at positions 6 or 7, induces a bathochromic shift in the emission wavelength curve (Fig. 2).³⁹ A vast majority of fluorescent chemosensors employing coumarin as a key group in combination with other functional receptors has been designed. Particularly, the coumarin moiety positioned at the 3- and 7-positions frequently serves as the structural backbone of the fluorophore, which has been widely used to monitor the distribution and concentration of ions, hormones and amino acids in plants, as well as assessing the quality of the soil in their living environment (Table 2).40

3.1.1 Fluorescent chemosensors derived from coumarin at 3-position or 7-position. Fluorescent coumarin derivatives at the 3-position or 7-position have been developed for detecting the distribution and concentration of ions and phytohormone in plants (Fig. 3). In 2021, Zhang et al. developed a coumarin derivative-based fluorescent chemosensor (1) linked by a Schiff base using straightforward synthesis and post-processing methods (Fig. 3a). 1 notably demonstrated remarkable aggregation stimulated luminescent amplification properties in the solvent environment (V_{HEPES}: V_{EtOH}), which was comprised of up to 40% aqueous portion. It showed proficiency in discerning the extraneous Zn²⁺ present within plant cells, exhibiting enhanced yellow-green fluorescence intensity at 515 nm (approximately two-fold) with a limit of detection (LOD) of

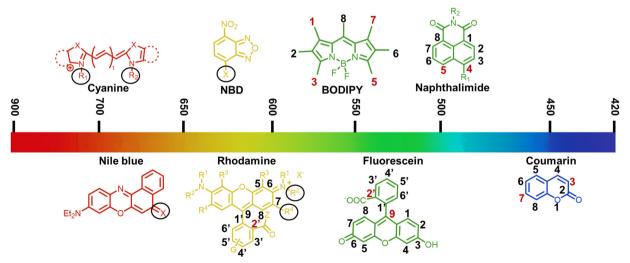


Fig. 2 Emission wavelength of small-molecule fluorescent chemosensors used in monitoring plant health. The fluorescent parents mainly include coumarin, naphthalimide, rhodamine, fluorescein, NBD, BODIPY, Nile bule, and cyanine. The numbers in red or black circle in the structure of the fluorescent parents are the modification sites for the fabrication of fluorescent chemosensors

Fluorescent coumarin derivatives for monitoring plant health and their environment

Chem Soc Rev

Classifications	Chemosensors $\lambda_{es}/\lambda_{em}$ (nm)	$\lambda_{ m ex}/\lambda_{ m em}~({ m nm})$	Solvents	Limit of detection (LOD)		Target analytes Applications	Ref.
Coumarin derivatives at 3-position Coumarin derivatives at 7-position	1 2	425/515 365/460	V_{HEPES} : $V_{EtOH} = 1:1$, pH = 7.0 0.0260 μ M Verhylene glycol: $V_{PBS} = 1:9$, pH = 7.3 52.0 ppb	$0.0260 \mu M \text{Zn}^{2+}$ 52.0 ppb Ethyl	Zn ²⁺ Ethylene	Detecting exogenous Zn ²⁺ in plant cells Monitoring endogenous-induced changes in ethy- lang higginghesis in plant	41
Coumarin derivatives at 3- and 7-positions	3	372/461	ЕтОН	1	Lignin	Visualizing the cell wall lignification process by labeling lignin	43
	4	428/505	V_{DMSO} : $V_{PBS} = 99$: 1, pH = 7.4	0.930 μМ	Cysteine	Detection of endogenous cysteine activities under external stimuli in live nematode and plant	44
	ıc	450/540-480	Aqueous solution	I	HClO	Tacking of exogenous/endogenous HClO variations 45 in plant cell	45
	9	410/480	V_{CH_3OH} : $^{3}_{3}V_{PBS} = 4:6$, pH = 7.4	0.220 μМ	$^{-}$ CN $^{-}$	Detecting CN in flaxseed and bamboo shoots, and	46
		620/745				monitoring the viscosity of introcholiuma	

 $0.026~\mu M.^{41}$ Another fluorescent coumarin derivative at the 7-position was developed by Chen *et al.* (2021) to monitor ethylene for evaluating the physiological state of plants (Fig. 3b). The fluorophore-tethered Rh^{III}-based fluorogenic coumarin-ethylene chemosensor 2 exhibited superb sensitivity (LOD = 52 ppb) and instantaneous identification of ethylene in air (<2 min).

Upon reacting with ethylene, an associated organic activation process was verified, displacing rhodium to form a novel fluorescent entity, thereby manifesting the maximum fluorescence intensity at the mid-wavelength of 460 nm. Moreover, 2 showed superior ethylene selectivity, effectively avoiding potential interference from diverse unsaturated plant metabolite molecules. Given the pivotal role of ethylene in pathogen defense and external stress responses, this chemosensor not only offers a significant mechanism for deepening our comprehension of ethylene biosynthesis regulation and ethylene signaling transduction in plants, but also enables the monitoring of pathogen infections, which can provide guidance for preventing pathogen infection and studying the physiological process of ethylene in real time.42 Coumarin-based fluorescent derivatives located at the 3- or 7-positions are expected to improve the emission spectrum for tracking small physiological molecules within plant cells. Furthermore, it is preferable for these probes, utilizing the coumarin fluorophore, to exhibit good water solubility.

3.1.2 Fluorescent chemosensors based on 3- and 7-positions of coumarin. Considerable effort has also been dedicated to exploring alternative positions of coumarins in fluorescent chemosensors targeting specific analytes. Four fluorescent chemosensors based on the 3- and 7-positions of coumarins can monitor plant components to evaluate plant health. The dimethylaminocoumarin-tagged guaiacyl monolignol chemosensor 3 was synthesized via a series of monolignol analogs γ-linked to fluorogenic aminocoumarin and nitrobenzofuran dyes, which could be inserted into the woody cell wall through a transpirational stream and biochemically integrated into lignins (Fig. 4a). Also, 3 showed high water solubility and membrane penetration, which was accurately and effectively reflected by staining unlabeled monolignol in plant tissue and the increase in fluorescent intensity at 461 nm, indicating its precise depiction of the integration of native lignin precursors, and hence monitoring tissue wall lignification processes in plants. This chemosensor is a useful tool for detecting the activity of lignification enzymes without destroying the plant environment and physiology, which is an important indicator for reflecting root ripeness and plant defense.⁴³ In 2019, Chen et al. reported the synthesis of fluorescent chemosensor 4 by integrating an acrylic acid ethyl ester moiety at the 3-position in the coumarin framework. This chemosensor exhibited high sensitivity towards cysteine (Cys) levels and activities with an LOD of 0.93 µM (Fig. 4b). The reactive thiol group of Cys could efficiently destroy the acrylate functionality through ring-closure reactions, generating a green fluorophore and ensuring an increase in fluorescence intensity at 505 nm. The dynamic alterations in the cellular Cys pool after exposure to oxidative stress triggers could be tracked using 4 in plants and nematodes, making it a significant diagnostic acid in probing the role of Cys in diverse biological events.44 Longer emission wavelengths are beneficial for

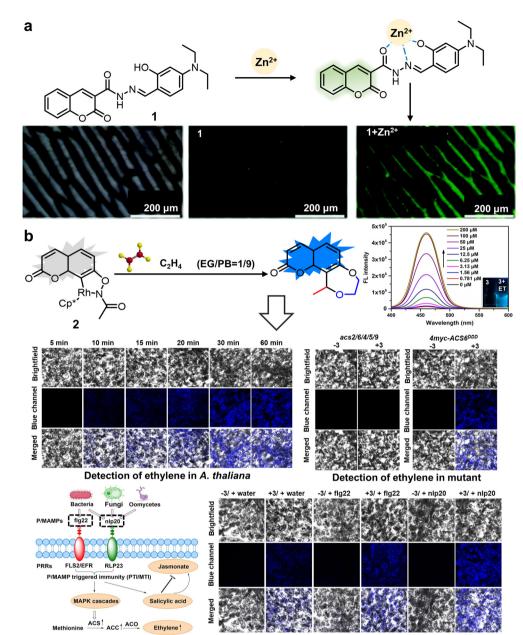


Fig. 3 Structure and application of fluorescent chemosensors 1 and 2 based on the 3-position or 7-position of coumarin for observing ions and hormones in plants. (a) Fluorescent chemosensor 1 synthesized using coumarin-2-hydrazine carbonate and 4-(diethylamino)-2-hydroxy-benzaldehyde can be used to monitor exogenous Zn²⁺ in plants.⁴¹ Reproduced from ref. 41 with permission from The Royal Society of Chemistry. Copyright © 2021, The Royal Society of Chemistry. (b) Chemosensor 2 constructed utilizing the 7-position of coumarin, affording monitoring of stress-induced changes in ethylene biosynthesis and ethylene signal transduction.⁴² Copyright © 2021, Wiley.

Detection of ethylene for monitoring pathogen infection

detection imaging given that they aid in reducing interference from background signals. In 2021, Wang et al. designed a highly specific colorimetric and ratiometric fluorescent chemosensor 5 comprised of coumarin aldehyde and HBT moieties. This chemosensor was responsive to HClO within 100 s due to the cleavage of the C=N bond (Fig. 4c). It sensed changes in extracellular or endogenous HClO levels inside plant cells within a short period (<100 s), causing a blue shift in fluorescence from the original green fluorescence (peak at 540 nm) to novel blue emission (peak at 480 nm). The LOD of 5 for the detection of HClO was 545 nM.

5 functioned as both a colorimetric and ratiometric chemosensor, enabling the imaging detection of HClO across diverse model systems. This highlights its broad spectrum of potential applications in the realm of plant science. 45 In 2023, Pan et al. developed a dual-responsive coumarin-derived NIR fluorescent chemosensor 6 for the simultaneous quantification of mitochondrial viscosity and cyanate (CN⁻). This chemosensor was synthesized using coumarin by expanding its double bond and linking benzindoles to enhance its conjugated structure (Fig. 4d). The significant increase in inner mitochondrial viscosity impeded the C=N bond rotation and

Fig. 4 Structure and application of fluorescent chemosensors 3-6 based on the 3- and 7-positions of coumarin for monitoring the growth and components of plants. (a) Fluorescent chemosensor 3 can accurately detect the concentration of lignin to monitor plant cell wall lignification. 43 Copyright © 2013, Wiley. (b) Fluorescent chemosensor 4 can monitor cysteine changes in plants and nematodes under stress-induced oxidative stress. 44 Copyright © 2019, The Royal Society of Chemistry. Reproduced from ref. 44 with permission from The Royal Society of Chemistry. (c) Fluorescent chemosensor **5** can detect the concentration of HClO in plants. ⁴⁵ Copyright © 2021, Elsevier. (d) Fluorescent chemosensor **6** can detect CN⁻ under different viscosity in the mitochondria in plants. 46 Copyright © 2023, Elsevier.

480 nm

disrupted the organized conjugated system, thereby leading to a characteristic redshift of 125 nm (from 620 nm to 745 nm). Monitoring CN levels also resulted in the enhanced excitation of the chemosensor with peaks at the wavelength of 410 nm and 620 nm, which was caused by the nucleophilic addition reaction between the chemosensors and CN-, disrupting the conjugated system and triggering a blue shift (410 nm/480 nm) at an LOD of 0.22 µM. Thus, 6 shows great promise for detecting CN⁻ under different mitochondrial viscosities in plants.⁴⁶ According to the

proposed interaction mechanism, the carbonyl groups of the dicarboximide moiety with N2H4 resulted in liberated aromatic amines, which induced appreciable fluorescence shifts. These fluorescent chemosensors exhibited a large Stokes shift for fast response and high-selectivity monitoring of plant cell growth and the physiological state of mitochondria. Fluorescent chemosensors originating from the coumarin fluorophore have found extensive use in monitoring and imaging plant tissues and samples. Nonetheless, they have some limitations, such as longer emission wavelengths,

elevated hydrophilicity, and minimal biological toxicity. Hence, the development and utilization of multifunctional fluorescent sensor materials, leveraging coumarin fluorophores with simple structures, versatility and high performance can facilitate the convenient detection of small molecule signals in plants.

Coumarin derivatives at the 3- and 7-positions have some advantages such as high solubility, photostability and large Stokes shift, and thus have been used for monitoring the health and living environment of plants. However, coumarin fluorescent chemosensors have certain drawbacks including high synthesis cost, complex synthesis process and environmental pollution. Therefore, further studies should focus on finding some new synthesis sites, recognition sites and mechanisms of action.

3.2 Naphthalimide derivatives

Review Article

The naphthalimide family represents a traditional class of D- π -A fluorophores, wherein the naphthyl nucleus functions as a π bond, R1 denotes an electron donor moiety, and the imide fragment functions as an electrophilic region.⁴⁷ Naphthalimides inherently exhibit electron-deficient characteristics. Given the facile N-functionalization of the 1,8-naphthalic anhydride progenitor via the Gabriel phthalimide methodology, most of the existing reports in the literature focused on substitution reactions of non-polar alkyl substituents, leading to imide linkages, and thereby enhancing the solvent compatibility. Furthermore, there are some alternative reactive sites within the naphthalene moiety (Fig. 2), 48 which can be readily modified to achieve a large Stokes shift, superior fluorescence OY and exceptional photostability. Notably, the 4-position has predominantly been subjected to manipulations due to its convenience in synthesis and diminished synthesis costs (Table 3). These chemosensors have been widely utilized for detecting ions, amino acid, pesticides, and pathogens in plants, as well as the quality of soil and water.

3.2.1 Fluorescent chemosensors based on 4-position derivatives of naphthalimide. The absorption and emission wavelengths of naphthalimides can be adjusted by altering the structure of the donating moiety, which is typically attached to the 4-position of the unit. Eight fluorescent naphthalimide derivatives at the 4-position were reported to evaluate the plant physiological status and irrigation water quality. In 2020, a twophoton (TP) ratiometric fluorescent chemosensor 7 was developed, which featured a TP fluorophore as the donor, an FA turnon naphthalimide fluorophore as the acceptor, and a brief hydrazide linker (Fig. 5a). It displayed remarkable speed in detecting formaldehyde, exhibiting high sensitivity and exceptional selectivity within 65 s. Its noteworthy features included a 60-fold amplification at 550 nm (ex = 700 nm) and impressive LOD of 5.8 nM. Furthermore, 7 possessed good imaging resolution and deep tissue penetration, which are valuable for investigating the formaldehyde dynamics in living onion tissues through intramolecular charge transfer (ICT) and photoinduced electron transfer (PET).49 In 2022, Kusano et al. synthesized a series of novel 1,8-naphthalimide-based chemosensors capable of selectively illuminating major subcellular structures such as the

Fluorescent naphthalimide derivatives for monitoring plant health and their environment Table 3

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Classifications	Chemosensors $\lambda_{\rm ew}/\lambda_{\rm em}$ (nm) Solvents	$\lambda_{\rm ex}/\lambda_{\rm em}~(\rm nm)$	Solvents	Limit of detection (LOD) Target analytes	Target analytes	Applications	Ref.
Naphthalimide derivatives at 4-position	7	760/410, 550	$760/410, 550 \text{ V}_{\text{DMSO}}$: $\text{V}_{\text{PBS}} = 1:99$	5.80 nM	Formaldehyde	Investigating formaldehyde in living onion tissues	49
•	8	405/540	Phosphate buffer solution, pH = 7.2	1	Plant intracellular compartments	Precise monitoring of subcellular behavior within the autophagic pathway	20
	6	420/560	$V_{PBS}:V_{DMSO} = 8:2, \\ pH = 7.4$	16.3 nM	Cysteine	Detecting cysteine in plant roots, food samples 51 and environmental water samples	51
	10	440/545, 565 Aqueous	Aqueous solution	I	The aggregation of anionic surfactants and bacteria	Monitoring the presence of cell membranes and 52 bacteria	52
	11	420/520	Aqueous solution	I	Reduction products of azole in bacteria	Investigating the microbial degradation and transformation mechanism	53
	12	390/510	$\label{eq:VCH_3CN:VHEPE} \begin{split} V_{\mathrm{CH_3CN}} \colon & V_{\mathrm{HEPE}} = 4:1, \\ pH &= 7.4 \end{split}$	V _{CH₃CN:V_{HEPE} = 4:1, 6.60 nM for mesotrione, pH = 7.4 7.37 nM for tembotrione, 10.2 nM for NTBC}	HPPD inhibitors	Detecting HPPD inhibitors including mesotrione, tembotrione and NTBC in soil and water	54
	13	380/550	Acetonitrile		_ H	Detecting F ⁻ content in tea leaves and water	22
	14	420/520	Tris-HCl, pH = 7.01	2.00 nM	${ m Hg}^{2+}$	Monitoring the concentration of Hg^{2^+} in river water	26
Naphthalimide derivatives at 5-position	15	365/511	Aqueous solution	0.490 nM	2,4- Dinitrophenylhydrazine	The detection of 2,4-dinitrophenylhydrazine in real water and soil samples	27
•	16	440/532	Aqueous solution	73.0 nM	${ m Hg}^{2+}$	Recognition of Hg ²⁺ in actual water, soil samples	28

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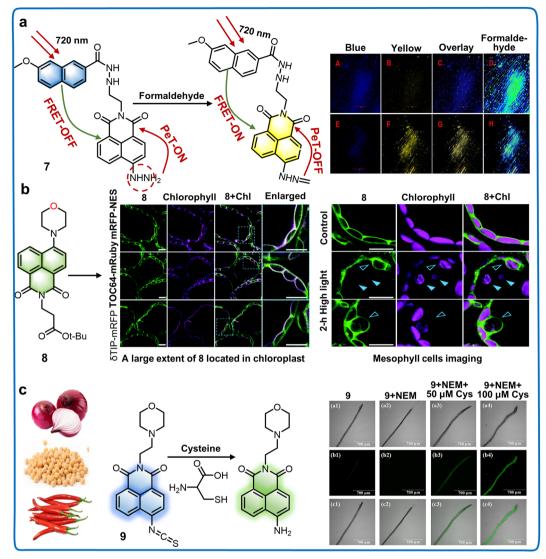


Fig. 5 Structure and application of fluorescent chemosensors 7-9 based on the 4-position of naphthalimide to monitor the subcellular structure and amino acid concentration in plants. (a) Fluorescent chemosensor 7 can detect formaldehyde rapidly in plants. (a) Copyright © 2023, Elsevier. (b) Fluorescent chemosensor 8 is capable of supervising the dynamic responses of plant organelle behaviors within an autophagic physiological process. 50 Copyright © 2021, The Royal Society of Chemistry. Reproduced from ref. 50 with permission from The Royal Society of Chemistry. (c) Concentration of cysteine in plants, food and water can be detected by fluorescent chemosensor 9.51 Copyright © 2023, Elsevier.

vacuolar membrane, the chloroplast envelope, and vacuolar lumen by modulating their spectral profiles (Fig. 5b). Among the chemosensors, the morpholino-substituted 1,8-naphthalimide (chemosensor 8) demonstrated rapid cell wall permeation and subsequent accumulation in the chloroplast, allowing the examination of the chloroplast dynamics given that the degraded chloroplasts transported into the vacuolar lumen via chlorophagy remained unstained. These fluorescent chemosensors enabled the real-time assessment of organelle behaviors within an autophagy pathway.⁵⁰ In 2023, a novel lysosome-directed Cys fluorescent chemosensor (9) was synthesized by incorporating an isothiocyanate moiety as the Cys recognition site within the naphthalimide fluorophore and integrating it with a morpholine moiety for lysosomal targeting (Fig. 5c). 9 exhibited a large Stokes shift (420 nm → 560 nm), negligible cytotoxicity, and

marked selectivity for detecting Cys in plant roots, food samples and water samples with an LOD of 16.3 nM. The Stokes shift of 9 decreased the background interference, which increased its detection accuracy and sensitivity.⁵¹ By incorporating an azetidine moiety in the aromatic nucleus of 10, it served as an electron-donating structural element, and strategically locating a hydrophilic (2-(2-aminoethyl-amino)ethanol) moiety within the "N-imide site" of the core structure (Fig. 6a). This chemosensor showed enhanced fluorescent intensity at 560 nm, making it well suited for tracking the assembly pathway of negatively charged surfactants, which is primarily ascribed to its exceptional surface accumulation property. Meanwhile, it was effectively utilized to detect bacteria and cell membranes by exploiting their negatively charged surfaces, thus serving as essential tools for the rapid measurement of biological contamination in water. These results

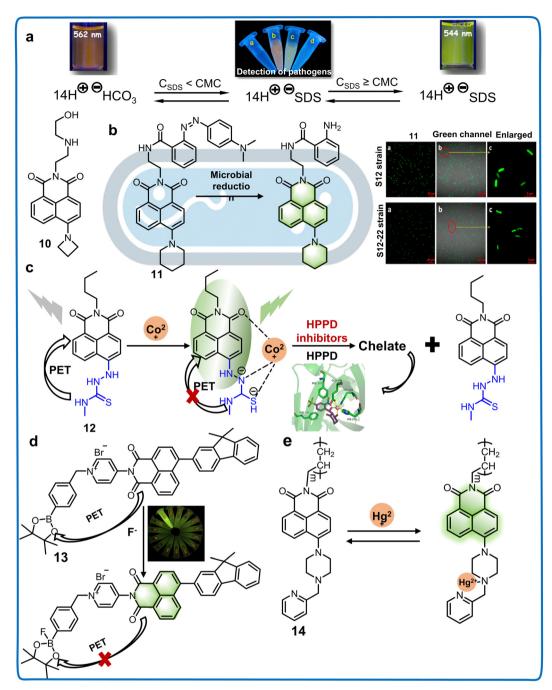


Fig. 6 Structure and application of fluorescent chemosensors 10-14 based on 4-position of naphthalimide to detect the pathogens, pesticides and ions in the living environment of plants. (a) Fluorescent chemosensor 10 can detect cell membranes of bacteria by detecting the viscosity and polarity of the medium. 52 Copyright © 2017, the American Chemical Society. (b) Fluorescent chemosensor 11 is a useful tool for understanding the degradation pathways of azo dyes in different microbial systems.⁵³ Copyright © 2015, the American Chemical Society. (c) Fluorescent chemosensor 12 exhibits remarkable potential for precisely detecting residual levels of HPPD inhibitors in water. 54 Copyright © 2021, Elsevier. (d) Fluorescent chemosensor 13 can detect F⁻ content in foods.⁵⁵ Copyright © 2022, Elsevier. (e) Fluorescent chemosensor **14** has a highly selective to response to Hg²⁺ in real water samples.⁵⁶ Copyright © 2013, Elsevier.

indicated that 10 has high potential for detecting microbial diversity in the living environment of plants.⁵² Fluorescent chemosensor 11 designed based on 1,8-naphthalimide and azo dyes can trace the microbial degradation routes of azo dyes via fluorescence resonance energy transfer (FRET) (Fig. 6b). In Pseudomonas stutzeri, its inherent attributes such as low polarity

and hydrophobicity of the azo dye allowed it to be internalised within cells, where it underwent reduction processes, while the relatively more polar and hydrophilic azo dye was relegated to reduction outside the cells. This phenomenon could be observed by the changes in fluorescence from darker yellow to brighter yellow. This chemosensor can pioneer a novel research models

for investigating microbial degradation and transformation mechanisms through the utilization of chemical fluorescentlabeling technology, which can provide guidance for engineering bacteria modification.⁵³ In 2021, the compound N-n-butyl-4methylhydrazinecarbothioamide-1,8-naphthalimide (chemosensor 12) was exclusively formulated and successfully manipulated to detect Co²⁺, affording an exceptional LOD of 7.82 nM through its fluorescence-on response. As illustrated in Fig. 6c, this was achieved by employing a fluorescent complex, namely NMN-Co²⁺, as a tool for identifying specific herbicide products known as HPPD inhibitors. Excitingly, these compounds exhibited a novel "turn-off" response with their sensing mechanism involving a competitive interaction between the chemosensor and HPPD in conjunction with Co²⁺. Notably, the corresponding LODs for NTBC, tembotrione, and mesotrione (HPPD inhibitors) were 10.22 nM, 7.37 nM, and 6.60 nM in water and soil samples, respectively. NMN represents the first fluorescent probe to be employed for discerning HPPD inhibitors with exceptional selectivity and sensitivity, offering a promising avenue for detecting the residues of triketone HPPD inhibitors.⁵⁴ In 2022, a fluorescent chemosensor (13), constructed from 1,8-naphthalimide and an organoboron compound (4,4,5,5-tetramethyl-2-phenyl-1,3,2dioxaborolane), functioning as a putative receptor of F-, was identified (Fig. 6d). The robust Lewis acidic boron moiety of 13 enabled tight coordination with basic F-, and then inhibiting

direct PET linkage from the fluorophore to the boron site, thereby

elevating the fluorescence emission at 540 nm. The LOD of **13** for F⁻ was established as exceedingly low at 33 nM, which could be effectively applied for detecting F⁻ in tea leaves and water.⁵⁵ Additionally, naphthalimide fluorescent chemosensor **14** endowed with a terminal double bond was formed following reaction with an appropriate organoboron compound. The post-modification step involved photo-crosslinking with 2-hydroxyethyl methacrylate on a glass surface (Fig. 6e). It was applied for the quantification of Hg²⁺ in river water at 520 nm with an LOD of 2 nM.⁵⁶ Continued research may unveil more naphthalimide derivatives with superior capabilities in detecting and monitoring an extended range of hazardous substances in the environment, thereby promoting favorable conditions for plant growth.

3.2.2 Fluorescent chemosensors based on 5-position derivatives of naphthalimide. Modifications at alternative sites of naphthalimide have also been devised for the synthesis of fluorescent probes for plant-related detection. Two fluorescent naphthalimide derivatives at the 5-position were developed to evaluate the soil quality in the living environment of plants. "Turn-off" fluorescent chemosensor 15 was constructed by utilizing chitosan as its skeleton and naphthalimide as the fluorophore, which remarkably showed a distinct response to 2,4-dinitrophenyhydrazine (DNPH) in river and soil extracts, leading to a change in fluorescence color from green to colorless (Fig. 7a). The LOD for DNPH was equated to a threshold of 0.49 nM.⁵⁷ Another chitosan-naphthalimide fluorescent chemosensor 16 was

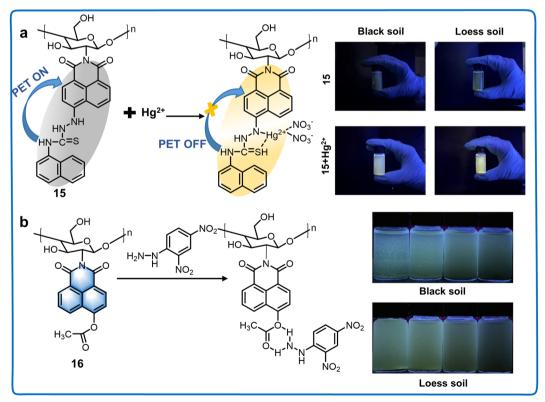


Fig. 7 Structure and application of fluorescent chemosensors **15** and **16** based on 5-position of naphthalimide for monitoring the quality of soil in the living environment of plants. (a) Fluorescent chemosensor **15** can be applied for the quantification of Hg²⁺ in irrigation water.⁵⁷ Copyright © 2021, Elsevier. (b) Fluorescent chemosensor **16** can monitor the concentration of DNPH in soil samples.⁵⁸ Copyright © 2023, Elsevier.

synthesized based on chitosan and 4-bromo-1,8-naphthalic anhydride, which exhibited no fluorescence in the solution phase initially (Fig. 7b). Upon the detection of Hg²⁺, an appreciable enhancement in fluorescence emission at 532 nm was observed, presenting a transformation from colourless to bright luminous yellow. This sensor displayed optimal properties with an LOD of 73 nM for recognizing Hg²⁺ in actual water and soil samples.⁵⁸ Furthermore, this type of fluorescent chemosensor could be used for monitoring the ion levels in plants and their response to external stresses owing to its good water solubility. As a result, environmentally friendly fluorescent chemosensors utilizing naphthylimide fluorophores have been developed, broadening the application scope of natural materials such as chitosan. These advancements have also aided in the development of fluorescent chemosensors for the detection of toxic substances over prolonged periods, allowing the observation of alterations in environmentally hazardous compounds.

Currently, 4-position naphthalimide derivatives with the advantages of photostability and good two-photon properties have been applied for monitoring plant health. However, are also some disadvantages to overcome, as follows: (i) the active site of naphthalimide is the 4-position, which limits the diversity of fluorescent chemosensors. Thus, to increase their diversity, novel recognition groups and various substituent units should be investigated. (ii) The low water solubility of naphthalimide derivatives decreases their sensitivity and responsiveness. (iii) The unstable and poor heat resistance of naphthalimide derivatives limit their application scope and accuracy.

3.3 Rhodamine derivatives

Rhodamine derivatives, part of the xanthene family together with fluorescein and eosin dyes, function as fluorophores with spectra relatively unaffected by pH changes within the range of 4-10.⁵⁹ Discovered in 1887, they have diverse applications in biotechnology, acting as fluorescent markers and aiding in the detection of small-molecules.⁶⁰ Since 1945, rhodamine-based chemosensors, capitalizing on analyte-induced spirolactam opening, have been designed for detecting metal ions and other biologically relevant species. 61 Rhodamine dyes, with moderate hydrophilicity, high absorption coefficient, elevated fluorescence QY, exceptional photostability, and visible light emission, have evolved beyond basic fluorescent labeling reagents into advanced fluorescent chemosensors.⁶² This section focuses on rhodamine-derived chemosensors, especially those targeting the health and living environment of plants (Table 4).63 The classical rhodamine dyes are predominantly employed in these applications, although in recent years, diverse modifications of rhodamine scaffolds have been performed for the visualization of plant components (Fig. 2).

3.3.1 Fluorescent chemosensors based on Z-position derivatives of rhodamine. Fluorescent chemosensors, utilizing Zposition rhodamine derivatives, have been extensively applied in detecting plant physiological signals and environmental parameters. For the detection of plant hormones, chemosensor 17, employing rhodamine Z-position derivatives, showed

remarkable sensitivity with an LOD of 1 nM for salicylic acid (SA) (Fig. 8a).64 It effectively detected the distribution and concentration of SA in plant callus tissues, serving as a sensitive tool for monitoring plant physiological states. Due to its promising performance and potential applications, 17 warrants further investigation for monitoring salicylic acid (SA) in the plant kingdom. This exploration may unveil novel immune activators for plant protection. For the detection of ions, an NIR fluorescence chemosensor (18) was engineered using the excellent fluorescence response platform of rhodamine dye, with a red-shifted emission wavelength to 695 nm (Fig. 8b). 65 Spectral experiments confirmed its fast response and high selectivity to Hg2+, finding applications in the biological domain, particularly in plant cells. The long emission wavelength of 18 suggested that it has high potential for monitoring the concentration of ions in plant tissues owing to its deep tissue penetration and low background interference. The synthesis of a reversible Al³⁺-specific fluorescent chemosensor (19) involved the conjugation of rhodamine B and pyridine-3sulfonyl chloride, employing the molecular connector ophenylenediamine (Fig. 8c).66 This chemosensor exhibited exceptionally high sensitivity and a high selective response to Al3+, which was effective for detecting low concentrations of Al³⁺ in plant tissues. Similarly, an activatable fluorescent chemosensor, rhodamine-based chemosensor 20, was designed through an acylation reaction at high temperature (Fig. 8d).⁶⁷ Its reversibility with Fe3+ was confirmed by adding Na₄P₂O₇, proving useful for detecting Fe³⁺ in environmental water samples. Meanwhile, biological experiments confirmed that 20 could be used to detect Fe3+ in plant tissues, implying that 20 showed favorable water solubility and membrane penetration. with a 2-[(1H-pyrrol-2-ylmethyl)-(2-Chemosensor 21, pyridinylmethyl)amino]-tripodal receptor integrated in its structure, exhibited unique characteristics, including photophysical spectral modifications, possessing specific affinity for Co²⁺, a notably high association constant, accelerated metalchemosensor reaction rates, and "on-off" signaling reversibility, together with a wide operational pH range. It was utilized in tracking the assimilation and accumulation of Co²⁺ within root and shoot tissues of Hybanthus enneaspermus (Fig. 8e). The results implied that 21 may be a useful tool for studying the accumulation of ions in plants or tracing the translation of ions from the environment to plants.⁶⁸ Integrating Z-position rhodamine derivatives into smart devices further facilitated the remote monitoring of various ions in the field and plants. Fluorescent sensors based on Z-position rhodamine derivatives offer unparalleled advantages such as their versatility across various plant species and capacity to rapidly convert endogenously produced chemical signals into detectable optical signals.

3.3.2 Fluorescent chemosensors based on 2', Z-position derivatives of rhodamine. 2', Z-position rhodamine derivatives have been proven to be versatile for detecting hormones and ions in plants. A recent breakthrough was chemosensor 22, which was synthesized using benzothiazole and rhodamine, facilitating the visualization of SA in plant tissues. This chemosensor was proven to be effective in monitoring SA levels,

Ref.

89

Detecting Co^{2^+} in root and shoot tissues of plant

 Co^{2+}

0.148 µM 3.00 µM

 $V_{\text{EtOH}}: V_{\text{H,O}} = 1:1 \text{ (HEPES,}$ $I_{\text{THF}}: V_{\text{H}_2\text{O}} = 8:2$ (HEPES,

520/582

0.5 mM, $\tilde{p}H = 7.3$

500/580 565/590

1.00 nM $0.0770 \mu M \text{ for Hg}^{2+}$

 $0.170~\mu\mathrm{M}$ for S^{2-}

0.164 ppb

 $V_{Acetonitrile}: V_{HEPES} = 4:1,$

515/555 260/700

24

Z-position derivatives Rhodamine 2', R2,

Rhodamine 2' and

170/635

2'-position derivatives 25

R4-position and

pH = 7.4

 $I_{MeCN}: V_{H_2O} = 2:3$

 $V_{EtOH}: V_{H_2O} = 1:1$ 0.01 M, pH = 7.4

 \tilde{V}_{EtOH} : V_{PBS} buffer = 7:3, pH = 7.4

Salicylic acid (SA) Monitoring SA in plants and food $\rm Hg^{2^+}$ and $\rm S^{2^-}$ Detecting $\rm Hg^{2^+}$ in living cells, animals and plant tissues

Detecting As3+ from a series of wastewater specimens

Visualization of Hg²⁺ and Cu²⁺ in soil and plants

Cu²⁺ and Hg²⁺

 $29.0 \text{ nM for } \text{Cu}^{2+}$

biological systems local river and lake water/plant tissues

Detection of trace Al³⁺ ions in water and

Al3+ and F

 $1.63 imes 10^5 \ \mathrm{M}^{-1} \ \mathrm{for} \ \mathrm{S}^{2-}$

14.2 nM

distribution of SA in plant callus tissues

Detecting Hg²⁺ in plant cells

and S^{2-}

 Hg^{2^+}

 $0.340 \mu M \text{ for Hg}^{2+}$

 $V_{H,O}: V_{EtOH} = 5:1$ (HEPES,

18

2.0 mM, pH = 7.0 $V_{\rm EtOH}:V_{\rm H_2O}=1:2$

520/582

19 20

 $V_{methanol}: V_{H_2O} = 9:1$

554/578 520/695

Rhodamine Z-position 17

derivatives

Solvents

 $\lambda_{
m ex}/\lambda_{
m em}$

Chemosensors

Classifications

1.00 nM

Salicylic acid (SA) Detecting the concentration and

Applications

Farget analytes

Limit of detection

(LOD)

Fe3+ and Na4P2O7 The detection of Fe3+ in cells, and plant tissues

72

73

Detection of perillaldehyde in the leaves of plants Detection of Ni and PPh₃ in plant and surroundings

Perillaldehyde Ni and PPh₃

530/552 Ethanol 20.0 μM for Hg^{2+} 530,580/640 30% acetonitrile aqueous solution 26.2 nM

26 27

 Table 4
 Fluorescent rhodamine derivatives for monitoring plant health and their environment

with a rapid response time of less than 1 min, high sensitivity, photostability, and LOD of 1 nM. As the SA concentration increased from 0 to 1000 µM, the test strips changed color from colorless to pink, while the fluorescence color shifted gradually from blue to pink to purplish. This advancement holds promise for plant biology studies and effectively detecting excess SA in common foods such as grapes, bananas, and cucumbers, serving as a warning system for SA-sensitive individuals (Fig. 9a).⁶⁹ Another innovative design, chemosensor 23, based on thiooxo-rhodamine B, involved sulfiding rhodamine spironolactam carbonyl groups to thiocarbonyl groups (Fig. 9b).⁷⁰ This fluorescent chemosensor exhibited a traditional reversible "turn-off-on" response with a uniform 1:1 binding stoichiometry. Notably, its C=S functional group served as a recognition group for Hg^{2+} , achieving an LOD of 0.077 μ M. Its versatility extended to detecting Hg2+ in irrigation water and plant tissues. Chemosensors utilizing this fluorophore were utilized to detect and image cations, anions, and phytohormones in plant samples. Additionally, they have the potential to expand their application in plant health monitoring by detecting metabolites, reactive oxygen species (ROS), and other pertinent compounds. 3.3.3 Fluorescent chemosensors based on 2', R2, R4-positions

and 2'-position derivatives of rhodamine. 2', R2, R4-position rhodamine derivatives are widely used for monitoring and quantifying the active constituents within plant samples and environmental samples, exhibiting versatile applications. Paul et al. demonstrated the arsenic-induced cleavage of the spirolactam ring in a cleft-shaped, electronically enriched rhodaminederived chemoreceptor molecule, PBCMERI-23 (Fig. 10a).71 Chemosensor 24, derived from this structure, displayed a 2-fold optical response (chromogenic, colorless to reddish pink; fluorogenic, non-blooming fluorescence to yellow emission) via the ring-opening phenomenon of the developed chemoreceptor. It showed sparkling yellow illumination under a fluorescence microscope, confirming cell permeability and serving as a biomarker for intracellular investigation and As3+ imaging in plant samples. Erdemir et al. introduced red-emitting fluorescent chemosensor 25, characterized by a substantial Stokes shift (about 220 nm), incorporating isophorone and rhodamine moieties (Fig. 10b).⁷² This compound displayed outstanding linear responsiveness toward Thiram, Cu2+, and Hg2+ in real soil samples, with LODs of 72.0 nM, 29.0 nM, and 122.0 nM, respectively. Moreover, the complex formed between the chemosensor and Cu²⁺ enabled the visualization of Thiram residues on a leaf surface, demonstrating the versatility of a singular probe. Zhao et al. developed chemosensor 26, an innovative "turn-on" and dual-mode sensor platform for the quantification of perillaldehyde concentration (Fig. 10c).⁷³ Equipped with appropriate solid-state irreversible sensors, these diagnostic strips adeptly evaluated the level of perillaldehyde present in Perilla frutescens leaves, offering potential applications in smart agriculture. The modification of the benzene ring at the 2'-position of rhodamine derivatives facilitated the assessment of the living environment of plants, including irrigation water quality and soil condition. In response to the carcinogenic nature of nickel compounds, Wang

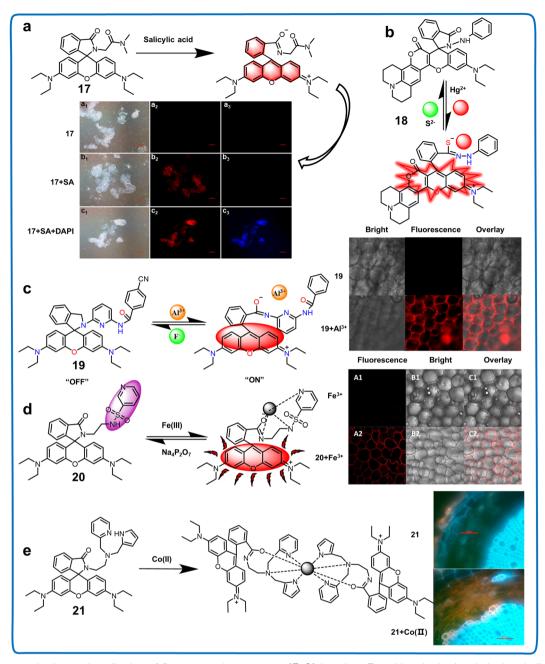


Fig. 8 Structure, mechanism and application of fluorescent chemosensors 17-21 based on Z-position rhodamine derivatives in live cell imaging. (a) Fluorescent chemosensor 17 can monitor the distribution and concentration of SA in plant callus tissues. 64 Copyright © 2020, the American Chemical Society. (b) Fluorescent chemosensor 18 can detect Hg²⁺ in plant cells. 65 Copyright © 2022, Elsevier. (c) Fluorescent chemosensor 19 can detect trace Al³⁺ ions in local river/lake water samples and plant tissues. 66 Copyright © 2020, Elsevier. (d) Fluorescent chemosensor **20** can monitor Fe³⁺ in cells, in vivo and plant tissues.⁶⁷ Copyright © 2020, Elsevier. (e) Fluorescent chemosensor **21** could be utilized for the detection of Co²⁺ in different plant tissues.⁶⁸ Copyright © 2016, Elsevier.

et al. developed chemosensor 27, an Ra-Ni ratiometric fluorescent chemosensor, sensitively detecting nickel ions with an LOD of 26.2 nM and rapid response (<2 min) (Fig. 10d).⁷⁴ Its practical effectiveness in actual water samples emphasized its utility in environmental applications. In summary, rhodamine derivatives located at the 2', R2, R4-positions, and the 2'-position offer efficient and simple tools for detecting ions, small molecules related to plant signaling, plant components, and pesticide residues. They present a novel and versatile approach for exploring physiological and pathological processes in plants. With their favorable performance, we anticipate the expansion of their applications for monitoring plant health.

Rhodamine derivatives have been widely used for monitoring the living environment and health of plants owing to their photostability, wide wavelength range and insensitivity to pH. However, they have some disadvantages, which should be

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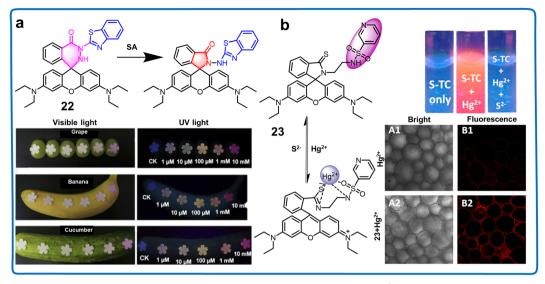


Fig. 9 Structure, mechanism and application of fluorescent chemosensors 22 and 23 based on 2', Z-position rhodamine derivatives in monitoring phytohormone and ions in plants. (a) Fluorescent chemosensor 22 can monitor SA in plants and food. ⁶⁹ Copyright © 2023, Elsevier. (b) Fluorescent chemosensor **23** can detect Hg²⁺ in plant tissues.⁷⁰ Copyright © 2019, Elsevier.

improved including (i) poor lipophilicity and poor penetration of cells, which make it difficult for in vivo imaging and (ii) low specificity and selectivity for specific binding, which decreases their detection accuracy. Thus, some specific recognition groups should be added to improve their selectivity.

3.4 Fluorescein derivatives

Fluorescein distinguishes itself as an eminently adaptable platform for diverse fluorescent chemosensors and markers, boasting high-intensity emission peaks, substantial molar absorption coefficients, and remarkable QY in aqueous media (Table 5).⁷⁵ Synthesized in 1871, fluorescein has gained significant attention and proven to be highly promising in various applications, particularly in smart sensors and bioimaging. The characteristic spirolactam structure of fluorescein enables a "close-open" transition with a "turn-on" fluorescence response in specific environments or events, making it an excellent dye for designing chemosensors.⁷⁶ Fluorescent chemosensors based on fluorescein offer the advantage of modification at two distinct moieties through organic synthesis, i.e., the xanthene ring and benzoic acid moiety (benzene moiety).⁷⁷ This structure enables modifications at the 2'-position, alterations to the hydroxyl group, or replacement of the oxygen atom at the 9-position (Fig. 2). Typically, most derivatives undergo modifications at these sites, enhancing the versatility of the fluorescein structure in designing functional and adaptable chemosensors (Table 5).

Fluorescent chemosensors based on the 2'-position of fluorescein can be used to image and monitor physiological signals in the field of plant research. Potter et al. utilized a 2'-position fluorescein derivative to exploit the thiol-dependent quenching of fluorescein isothiocyanate (FITC) in developing a sulfidespecific assay. This innovative approach employed a polydimethylsiloxane (PDMS) membrane (chemosensor 28), which is permeable to hydrogen sulfide while excluding larger charged

thiols (Fig. 11a).⁷⁸ They found that the formation of fluorescein dithiocarbamate (FDTC) upon reaction with sulfide could specifically interact with S-nitrosothiols (RSNO), regenerating FITC. This process acted as a specific, fluorogenic reagent capable of detecting picomolar levels of RSNO. These findings contribute to understanding the changes in plants induced by bio-thiols and peroxides.

Simultaneously, 9-position fluorescein derivatives have been applied in the detection of various plant components and signal changes in plants. In 2020, Takaoka et al. reported an innovative methodology involving fluorescence-imaging and utilization of fluorescein diacetate conjugated with Hoechst 33342, a well-known nuclear staining compound (chemosensor 29), facilitating the rigorous qualitative quantification of stoma dynamic responses (Fig. 11b).79 Using this method, the dynamic motion of stomata in Arabidopsis thaliana was interpreted through the straightforward surveillance of irregular changes in fluorescence intensity within the nuclear region of the stomata. The results indicated that 29 may be an alternative tool for regulating the drought response of plants or screening drought-resistant plants. Finally, a 9-position fluorescein derivative was valuable for the efficient detection of ions in food samples. Compounds functionalized with fluorescein and catechol (chemosensor 30), synthesized through a Schiff base reaction, exhibited recognition capabilities for ClO- in food items (Fig. 11c).80 Based on its excellent selectivity, high sensitivity (LOD of 36.3 nM), "fast" response time (15 s), and large Stokes shift (353 nm), 30 was employed to detect exogenous ClO in potato sprouts. These fluorescein derivatives can be employed to detect small active molecules that are challenging to capture and to track kinetic processes in plants. The anticipated advantages of employing fluorescein in objective analyses include enhancing the capability for high-throughput examination of chemical repositories. This facilitates the development of

Control pollen cell Cell with As Spiked soil samples (uM) b 25 Soil and Plant sample Scindapsus Ni(0) NaBH. Ni(0)

Fig. 10 Structure, mechanism and application of fluorescent chemosensors 24-27 based on 2', R2, R4-position and 2'-position rhodamine derivatives in soil samples and plants. (a) Fluorescent chemosensor **24** can detect As(\mathfrak{m}) in a series of water specimens. Copyright \mathfrak{Q} 2019, the American Chemical Society. (b) Fluorescent chemosensor **25** can be used for the visualization of Hg²⁺ and Cu²⁺ in soil and plant. Copyright \mathfrak{Q} 2023, Elsevier. (c) Fluorescent 26 can be utilized for the detection and evaluation of perillaldehyde in the solution phase and plant leaves. 73 Copyright © 2022, the American Chemical Society. (d) Fluorescent chemosensor 27 can detect Ni and PPh₃ in the living environment and tissues of plants.⁷⁴ Copyright © 2022, Elsevier.

innovative chemical chemosensors and provides insights into biosensors. The utilization of fluorescein-based chemosensors has the potential to deepen our comprehension of plant responses to environmental changes.

Fluorescein derivatives show high water solubility and QY but they also have some disadvantages, as follows: (i) their light stability is poor and their fluorescence is easily quenched after long irradiation. Further studies should focus on modifying and optimizing the structure of fluorescein derivatives to improve their stability. (ii) They are very sensitive to pH and their fluorescence intensity can change under different pH conditions, which decrease their application scope and detection accuracy.

NBD derivatives 3.5

In 1968, Ghosh and Whitehouse reported the synthesis of 4chloro-7-nitro-2,1,3-benzoxadiazole (NBD-Cl), an ingeniously conceived fluorogenic reagent exclusively engineered for the detection of amino acids and various amines. Since its discovery, compounds featuring the NBD framework are prevalent in biochemical studies and chemical biological explorations, marking their significance in various research domains.85 The

spectral range of the emission from N-monoalkyl NBD amines (NBD-NHR) extends beyond 420 nm, with their fluorescence arising from ICT transitions.86 In NBD-NHR assemblies, the amino function serves as the ICT donor, while the nitro site, a potent electron-withdrawing moiety, operates as the acceptor.⁸⁷ Notably, donor-acceptor (also known as push-pull)-type dipolar fluorophores generally exhibit strong emission in organic solvents but are often less effective in aqueous media due to the hydrogen bond interactions between water and the 2-oxa-1,3diazole moiety of NBD, leading to nonradiative dissociation channels. Consequently, NBD-NHR species in aqueous solutions tend to have lower QYs.88 However, the distinct advantages such as water solubility, eco-sensitivity, and concise dimensions of NBD-NHR fluorophores make them highly valuable, facilitating biomolecular interactions and self-assembly, especially in living systems (Table 5). The structural characteristics of the latter two compounds are commonly harnessed in

the visualization of plant health (Fig. 2). NBD derivatives are some of the most used fluorophores for live plant imaging owing to their simplicity, high efficiency, high sensitivity and low detection limits in fluorescence analysis. FluorA I and II, fluorescent conjugates of 2,4-D with NBD, served as promising auxin chemosensors (31), mimicking known auxin distribution patterns in distinct developmental processes. These conjugates displayed potential for visualizing auxin distribution in plant roots and apical hooks (Fig. 12a).81 Additionally, the probe revealed the presence of fluorescent analogues in specific organelles such as the ER and endosomes. This toolkit provided high spatiotemporal resolution support for elucidating the mechanisms governing the precise, local regulation of auxin distribution in living materials. Tobimatsu et al. reported the synthesis of a range of monolignol analogs, γ -conjugated with substrates such as fluorogenic aminocoumarin and nitrobenzofuran dyes (chemosensor 32), which were examined for potential application as imaging chemosensors. They proved to be valuable for visualizing the cell wall lignification process in A. thaliana and Pinus radiata under diverse feeding conditions (Fig. 12b).⁴³ An NBD derivative, chemosensor 33, was applied for the detection of pH, anions, cations, and biothiols in plants. 33 exhibited exclusive affinity for Hg²⁺ with an activation of emission wavelength at 543 nm. Its reversible fluorescence response, coupled with a low detection limit (19.2 nM) in the pH range of 6.0-7.5, positions NBDP as a prospective option for detecting Hg2+ in neutral aqueous settings. This phenomenon was attributed to the impediment of the photo-electron transfer (PET) mechanism upon complex formation with Hg²⁺ (Fig. 12c).⁸² This chemosensor with high water solubility was effectively employed for fluorescence imaging in plant tissue. Furthermore, NBDP demonstrated Hg²⁺ recognition ability in live tissues of A. thaliana via fluorescence imaging. NBD-NHR-based fluorescent chemosensors have been widely employed in plant detection. Yu et al. ingeniously devised a new molecular pH sensing agent, chemosensor 34 (NBD-pbz), which was formed through the strategic combination of 2-piperazin-1-yl-1,3-benzothiazole (pbz) and 7-nitro-1,2,3-benzoxadiazole (NBD) elementary units (Fig. 12d).83 34 enabled the precise monitoring of pH variations spanning the range of 3.2–7.6, demonstrating a pK_a

 Table 5
 Fluorescent fluorescein and NBD derivatives for monitoring plant health and their environment

Classifications	Chemosensors $\lambda_{\rm ew}/\lambda_{\rm em}$ (nm) Solvents	$\lambda_{ m ex}/\lambda_{ m em}~{ m (nm)}$	Solvents	Limit of detection (LOD)	Target analytes	Applications	Ref.
Fluorescein 2'-position 28	28	365/543	HEPES buffer (0.1 M,	200 pmol	S-Nitrosothiols and	Visualization of intracellular RSNO in plans seed-	78
derivatives Fluorescein 9-position 29	29	I	рн = 6.5) —	I	nyarogen sumae —	ing roots Assessment of stomatal dynamics in <i>A. thaliana</i>	62
derivatives	30	350, 507/650	350, $507/650$ $V_{H_2O}:V_{THF} = 7:3$	86.7 nM	Exogenous CIO	Monitoring of exogenous ClO in potato sprouts	80
NBD-N derivatives	31	ı	I	I	Auxin	and industrial effuents Visualising the distribution of auxin in plants at	81
	32	488/500-650	488/500-650 Aqueous solution	I	Monolignols	cellular or subcellular levels Understanding the plant cell wall lignification	43
	33	495/543	Aqueous solution	19.2 nM	${ m Hg}^{2+}$	process The Hg^{2+} recognition in live tissues of A. thaliana	82
NBD-O derivatives	34 35	450/540 480, 550/625	(containing 0.4% DMSO) 450/540 PBS buffer (1% DMSO) 480, 550/625 PBS buffer (pH = 7.4,	 0.0820 µM for GSH	pH Cys/Hcy and GSH	Tracking of pH changes in mung bean sprouts Detecting Cys/Hcy and GSH in A. thaliana	83
			containing 20% CH ₂ CN, v/v)				
				0.0610 µM for Cys/Hcy			

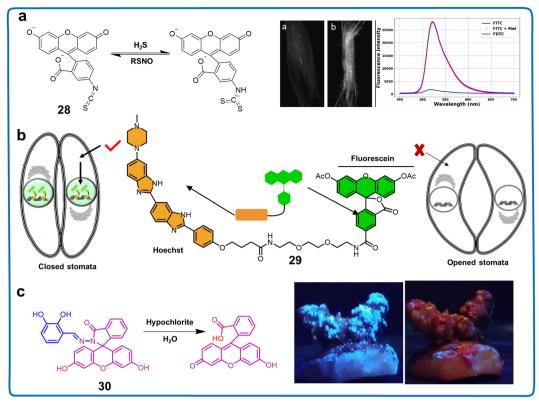


Fig. 11 Structure, mechanism and application of fluorescent chemosensors 28-30 based on 2'-position fluorescein derivatives in imaging water samples and plants. (a) Fluorescent chemosensors 28 for the visualization of intracellular RSNO in plant seedling roots. 78 Copyright © 2022, Elsevier. (b) Fluorescent chemosensors 29 is employed to assess the stomatal dynamics in *A. thaliana*. Oppright © 2020, Springer Nature. (c) Fluorescent chemosensors 30 for monitoring exogenous ClO⁻ in potato sprouts. 80 Copyright © 2023, Elsevier.

value of 5.51, as observed in mung bean sprout tissues. This functionality was enabled by utilizing a fluorometric activation response together with an ICT-based operating mechanism methodology. This type of structure was versatile for detecting anions, cations, and biothiols in environmental samples. Fluorescent chemosensors based on the 2-oxa-1,3-diazole of NBD were also extensively utilized in plant detection and could sensitively detect biothiols (such as amino acids or sulfide) in plants, real environments, and food samples. For instance, Huang et al. synthesized NBD-O-1 (chemosensor 35), which was capable of detecting endogenous compounds such as Cys/Hcy and GSH in A. thaliana (Fig. 12e).⁸⁴ The fluorescence emission amplitude of NBD-O-1 at 550 nm and 625 nm significantly increased upon exposure to Cys/ Hcy with superior selectivity and LOD of 0.061 μM. The experiment demonstrated the utility of 35 in exploring the conversion and metabolic pathways of thiols in plants. NBD, known for its low molecular weight, high QY, and stability, presents numerous advantages. It has found extensive use in plant imaging to observe physiological processes within plant cells. This effort seeks to enhance our comprehension of physiological processes from the standpoint of subcellular organelles in plants, which play an important role in plant health management. Hence, the introduction of NBD derivatives can provide a new perspective to study the changes of physiological signals within the plant system.

The low molecular weight, high solubility, biocompatibility and relatively easy synthesis process of NBD derivatives have led to their use in plant imaging. However, they also have some disadvantages, as follows: (i) their emission spectrum is located in the range of 500-560 nm, which overlaps with some spontaneous fluorescence in biological systems, causing fluorescence interference and (ii) the relatively low structural diversity of NBD derivatives limit their application scope. Thus, more substituent or recognition groups should be added to NBD.

BODIPY derivatives 3.6

The BODIPY molecule, also known as 4,4-difluoro-4-bora-3a,4adiaza-s-indacene, has been attracting increasing interest due to its minimal Stokes shift, substantial absorbance, narrow absorption and emission spectra, elevated QY, insensitivity to variations in polarity and pH, and consistent chemical structure and mechanism, making it a highly favored fluorescent dye. 89,90 Developed by Treibs and Kreuzer in 1968, research related to the BODIPY compound underwent a period of inactivity spanning over a decade, only regaining prominence in the late 1980s.91 In recent years, BODIPY has found extensive application in biochemistry, materials science, engineering, physics, electronics, therapeutic applications, and various other fields. The inherent adaptability of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene-based BODIPY derivatives allow significant alterations, making them optimal candidates for use as photodynamic therapy (PDT) agents, including low dark toxicities, cellular uptake, high extinction coefficients, and low photobleaching. This versatility allows for modifications,

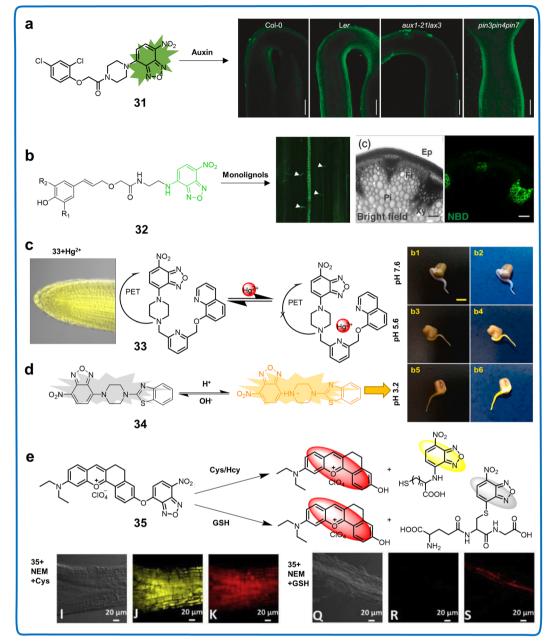


Fig. 12 Structure, mechanism and application of fluorescent chemosensors 31-35 based on NBD-N for visualising plant growth. (a) Fluorescent chemosensor 31 for visualising auxin distribution within different plant tissues at the cellular or subcellular levels. 81 Copyright © 2021, Wiley. (b) Fluorescent chemosensor 32 for understanding the intricacies of cellular wall lignification in plants. 43 Copyright © 2013, Wiley. (c) Fluorescent chemosensor 33 for Hg²⁺ recognition in live tissues of A. thaliana. 82 Copyright © 2020, Elsevier. (d) Fluorescent chemosensor 34 for tracking pH changes in mung bean sprouts. §3 Copyright © 2021, Elsevier. (e) Fluorescent chemosensor 35 for detecting Cys/Hcy and GSH in A. thaliana. 84 Copyright © 2019, Elsevier.

enabling absorbance at long wavelengths. 92 Acting as an acceptor, the optical properties of BODIPY can be finely tuned through facile structural modifications on its core. 93 The core of BODIPY allows functionalization at its meso-, α -, β -positions and B(III) center, and thus the introduction of substituents with varying electron densities and adjusting its conjugation length with suitable spacers or π -linkers (Fig. 2). The extensive synthetic methodologies and diverse functionalization options of BODIPY make it one of the most extensively studied organic fluorophores (Table 6).

3.6.1 Fluorescent chemosensors based on 3,5-position derivatives of BODIPY. Numerous 3,5-position BODIPY derivatives have played crucial roles in monitoring food security and plant components. Zhang et al. developed an innovative boratefunctionalized BODIPY-based fluorescent paper chemosensor (36) with heavy metal ion responsiveness employing solid phase extraction technology (SPE). 36 showed both superior selectivity and sensitivity in the quantification of minimal traces of Cd²⁺ in rice with an LOD of 0.5 µM, which is useful for monitoring

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Table 6 Fluorescent BODIPY, Nile blue, cyanine derivatives and chemosensors with AIE property for monitoring plant health and their environment

Review Article

100 101 102 103

Determining ArSH in industrial wastewater

Poxic thiophenol

Selenol

NaCl

170 and 448 µM

1.80 nM 9.50 nM

 V_{EtOH} : $V_{PBS} = 3:2$, pH = 7.4PBS buffer (10 mM, pH = 7.4) 0.540 nM

rriton X-100/HEPES buffer

340, 385/440,

620/675 652/692 680/790

44

Cyanine derivatives

0.9 = Hd

ACN

510, 640/;

520-800, 650-850

515, 637/816

300-350/675

492/614

48

with AIE property

Chemosensors

PBS buffer

Monitoring Salt Stress of plants

Monitoring CN in water

Detecting selenol in foodstuff

98

Imaging microviscosity in key plant cell structures Marking the level of ${\rm Hg^{2^+}}$ pollution in A. thaliana

Detection of Cd²⁺ in real rice samples

Applications

Target analytes

Limit of detection

 Cd^{2+}

0.500 µM

Aqueous solution

Solvents

Chemosensors $\lambda_{\rm ex}/\lambda_{\rm em}$ (nm)

36

BODIPY 3,5-position

derivatives

Classifications

Monitoring BRs epidermal cells of A. thaliana

Brassinosteroids (BRs)

Cys HPPD

11.2 nM HP-1 (0.700 μ g mL⁻¹

 V_{PBS} : $V_{CH_3CN} = 1:1$, pH = 7.4 PBS buffer (100 mM, pH = 7.4)

and 4.53 $\mu g \, m L^{-1}$) HP-2 (0.800 $\mu g \, m L^{-1}$ and 2.41 $\mu g \, m L^{-1}$)

Viscosity Mercury

 $2.66 \times 10^{-4} \text{ mol L}^{-1}$

 $V_{\rm H_2O}:V_{\rm DMF}=7:3$

640/790

37 38

BODIPY 1,3,5,7-position

derivatives

DMSO

495/505 505/600 580/675

40

Nile blue derivatives

39

Monitoring AtHPPD, HPPD of A. thaliana

Detecting Cys in food samples

105 106

Imaging the morphological changes of plasma membranes 107

Distinguishing the meristematic zone in root tissue

and primary xylem in stem tissue

Plasma membranes

Determination of BChE and detection of DDVP

DDVP residues

 $0.240~\mu g~mL^{-1}$

PBS buffer (10 mM, pH = 8.0

containing 15% DMSO)

Lignin

Phosgene

0.0800 ppb

residues in food samples

Monitoring phosgene in soil

104

food safety (Fig. 13a).⁹⁴ In 2020, Michels et al. introduced an imaging microviscosimetry toolbox (chemosensor 37) of molecular rotors, which was designed for the comprehensive microviscosity mapping of cells and tissues. These molecular rotors precisely targeted the cytosol, vacuole, plasma membrane, and cell wall of plant cells (Fig. 13b). 95 Operating based on BODIPY, these molecular rotors exhibited rigidochromicity, linking the rate of intramolecular rotation, influenced by their direct surrounding mechanics, with their fluorescence lifetime. Despite the typically low intracellular levels of physiological parameters in plants and environmental parameters, detecting them remains a challenge. In this case, the combination of fluorescent imaging with chemosensing exhibits unparalleled utility in plant experiments, yielding elevated sensitivity, direct on-site evaluation, and minimal damage. 3.6.2 Fluorescent chemosensors based on 1,3,5,7-position derivatives of BODIPY. The remarkable specificity and sensitivity of fluorescent chemosensors based on 1,3,5,7-position BODIPY

derivatives have fundamental advantages in botanical investigations. In 2022, Chen et al. innovatively utilized a BODIPY core as an NIR fluorophore, paired with an aza-containing macrocyclic thioether recognition ligand to create novel chemosensor 38 with outstanding photostability. 38 was employed for the specific recognition of Hg²⁺, emitting NIR light at 753 nm (Fig. 14a).⁹⁶ Importantly, its emission effectively avoided interference from chlorophyll fluorescence in A. thaliana, ensuring the accurate quantification of Hg^{2+} levels, with an LOD of 2.66 \times 10⁻⁴ mol L^{-1} . Fluorescence imaging of A. thaliana seedlings revealed that 38 can monitor the heavy metal pollution in plants, thus providing an efficient molecular tool for determining the Hg2+ levels and translocation in living biosystems. For the precise, noninvasive detection of brassinosteroids (BRs) in plants, Starodubtseva's team synthesized a BODIPY-conjugated epibrassinolide (chemosensor 39). 39 could not only assess bioactivity but also serve as a fluorescent tool for the in vivo visualization of BR. Mimicking the effects of eBL, this chemosensor is suitable for both short- and long-term applications and holds high potential for use in cell biology studies, especially it may be an effective tool for studying the physiological function of BR in plant resistance to biotic or abiotic stresses (Fig. 14b).97 In Cys detection, Yang et al. ingeniously synthesized "turn-on" fluorescent chemosensor 40 utilizing the BODIPY platform specifically for detecting Cys in food samples (Fig. 14c). 98 This chemosensor, with a brief reaction time (10 min) and distinctive color response (blue to pink), boasted a high signal-to-noise (S/N) ratio (3150-fold) and sensitivity (LOD = 11.2 nM) towards Cys. Conveniently deposited on test strips, it became a robust tool for analyzing the Cys levels in food samples and complex biological systems. Consequently, these dynamic molecules derived from BODIPY play crucial surveillance and visualization roles in the complex procedures of plant growth, development, and stress responsiveness. These chemosensors also have utility in detecting and visualizing hazardous substances, analyzing food and environmental samples, and studying intricate living systems.

The advantages of BODIPY derivatives include their favorable QY, high molar extinction coefficient, and insensitivity to Chem Soc Rev **Review Article**

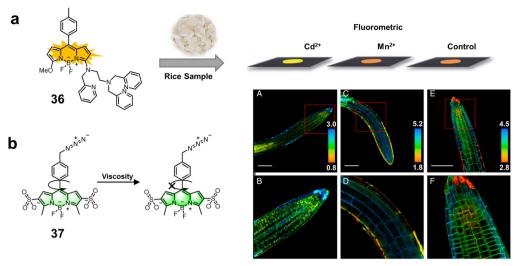


Fig. 13 Structure and mechanism of fluorescent chemosensors 36 and 37 based on 3,5-positions derivatives of BODIPY for monitoring ions and viscosity in plant cells. (a) Fluorescent chemosensor 36 for the specific quantification of Cd²⁺ in real rice samples. Copyright © 2014, The Royal Society of Chemistry. 94 Reproduced from ref. 94 with permission from The Royal Society of Chemistry. (b) Fluorescent chemosensor 37 for imaging microviscosity in key plant cell structures. 95 Copyright © 2020, PNAS.

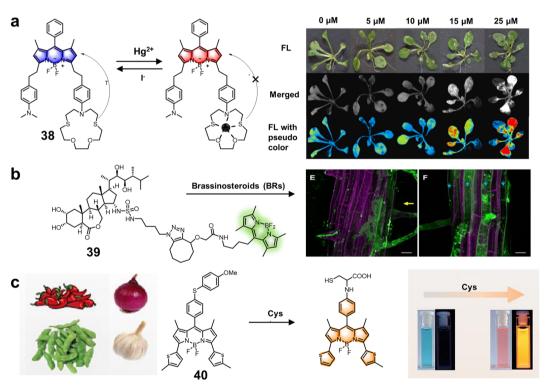


Fig. 14 Structure and mechanism of fluorescent chemosensors 38-40 based on 1,3,5,7-position BODIPY derivatives for the evaluation of ions, hormones and amino acids in plants. (a) Fluorescent chemosensor 38 for marking the level of Hg²⁺ pollution in A. thaliana. ⁹⁶ Copyright © 2022, Elsevier. (b) Fluorescent chemosensor 39 for monitoring BR epidermal cells of A. thaliana roots. 97 Copyright © 2021, MDPI. (c) Fluorescent chemosensor 40 for detecting Cys in food samples. 98 Copyright © 2023, Elsevier.

pH. However, they also have some disadvantages, as follows: (i) the low water solubility of BODIPY derivatives limits their application in in vivo imaging and (ii) their relatively low photostability and easy photobleaching can reduce their detection accuracy, which implies the important of timeliness of sample preparation.

Nile derivatives

Nile blue, discovered by scientist Lorrain Smith in 1908, serves to distinguish neutral fats, specifically staining fatty acids deep blue and triglycerides and steroids reddish-pink. It is comprised of oxazine sulfate (true Nile blue) and oxazone (Nile red) and is soluble in water and ethyl alcohol. 108 Nile pink, its

oxazone form, results from the spontaneous oxidation of Nile blue A in an aqueous solution or refluxing Nile blue A with dilute sulfuric acid (Fig. 2).109 It exhibits high solubility in neutral lipids, showing fluid characteristics at the required staining temperature. Although Nile blue is inherently hydrophobic, modifications to facilitate its water solubility are possible. 110 However, its synthesized analogs evaluated thus far show fluorescence in the NIR region with a low OY in aqueous systems or in the presence of proteins (Table 6).

4-Hydroxyphenylpyruvate dioxygenase (HPPD), which plays a pivotal role in the biosynthesis of vitamin E and plastoquinone in plants, has been regarded as a key herbicide target for over 30 years. Recently, it was recognized as a marker for plant health under abiotic stresses. Fu et al. introduced chemosensor 41, a tool for precise visualization and PL in in vivo studies, for the exceptionally effective identification of an HPPD-targeted inhibitor (Fig. 15a).99 41 exhibited an approximately 16-fold enhancement in fluorescence levels upon exposure to HPPD,

showing excellent specificity for imaging HPPD in complex environments. Importantly, it allowed the visual tracking of HPPD activity in plants spatially and temporally, overcoming the inconsistency between molecular-level HPPD-based bioevaluation and weed control efficiency.111 Zeng et al. proposed a fluorescence labelling method for HPPD, avoiding interference with normal plant growth. The innovative bioorthogonal strategy visualized HPPD in A. thaliana, integrating the evaluation of the adaptive response of plants to diverse abiotic stresses, while simultaneously monitoring the in vivo concentration and subcellular localization of HPPD in plants. Additionally, they executed a systematic molecular construction for a highly specific HPPD-reactive fluorescent chemosensor, demonstrating excellent capability for monitoring the presence of HPPD in A. thaliana and detecting dynamic fluctuations occurring under varying levels of temperature stress coupled with Cd²⁺ stress.¹¹² These results indicated that this chemosensor may be an effective tool for investigating abiotic stress mechanisms associated with HPPD,

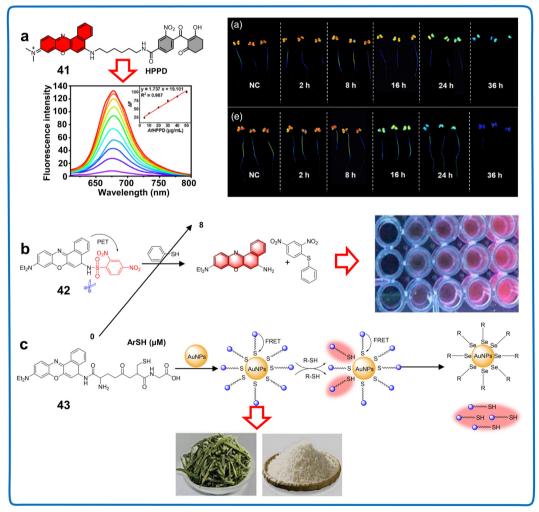


Fig. 15 Structure, mechanism and application of fluorescent chemosensors 41-43 based on Nile blue for monitoring water quality and plant components. (a) Fluorescent chemosensor 41 for monitoring AtHPPD, HPPD in A. thaliana. 99 Copyright © 2022, Wiley. (b) Fluorescent chemosensor 42 for determining ArSH in water. 100 Copyright © 2019, Elsevier. (c) Fluorescent chemosensor 43 for detecting selenol in foodstuff. 101 Copyright © 2020, Elsevier.

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detecting herbicidal compounds, evaluating enzymatic activity and elucidating uncharacterized biological functions.

The Nile blue fluorophore is extensively used in evaluating food and environmental samples. Wu et al. introduced an innovative NIR fluorescent chemosensor (42) for detecting thiophenols in environmental water samples. Through a single-step condensation process using 2,4-dinitrobenzenesulfonyl chloride in combination with Nile blue (Fig. 15b), this sensor demonstrated a remarkable chromogenic reaction and NIR fluorescent "turn-on" response against thiophenols, offering exceptional sensitivity, prompting a rapid response (12 minutes), and impressive LOD of 1.8 nM. 100 Nile blue-DN effectively monitored the thiophenol levels in water with good recoveries ranging from 90% to 110%, which offered a robust strategy for facilitating highly precise measurements of the thiophenol levels in environmental water samples. Further studies should explore the integration of 42 with enzyme-responsive groups, which can increase its pesticide detection sensitivity and reduce the complex processes for enzyme activity analysis. Nile blue is also employed for detecting components in food samples. Selenocysteine (Sec), a crucial reactive selenium species, was the focus of the study by Guo et al. They reported the synthesis of a chemosensor (43) comprised of oxidized glutathione (GSH) and Nile blue ligands immobilized in gold nanoparticles (AuNPs) (Fig. 15c). 101 The developed chemosensor displayed remarkable sensitivity and specificity towards Sec, facilitating the visualization of both endogenously present and externally administered Sec within plant cells via confocal fluorescence microscopy. This proposed analytical device hold substantial promise for the detection of selenol in foodstuffs such as selenium-rich rice and tea, exhibiting an impressive LOD of 9.5 nM, holding great potential for advancing the detection of selenol and unraveling its role in organisms. The results indicated that 43 can also be used as an indicator to analyze the redox balance in plants. Customizing these chemosensors for the precision targeting of distinctive biologically active compounds within plants, including reactive species, metal ions, signal-transducing molecules, and harmful substances, enables the precise and quantitative detection of these indispensable active substance.

Compared with other fluorescent chemosensors, NIR chemosensors have less background interference, strong tissue penetration and high solubility, making them more suitable for in vivo imaging. However, their rational structural modification, specific recognition groups and simple synthesis process should be explored to improve their specificity and sensitivity.

3.8 Cyanine derivatives

Cyanine (CY), a classical cyanine dye, features two nitrogencontaining heterocycles and a conjugated chain of methyl chloroform $(CH)_n$, with an odd or even number of n. Manipulating the length of the poly(hypomethyl)-bridge allows the control of its absorbance and fluorescence wavelengths, resulting in higher absorbance and emission wavelengths (Fig. 2). Quinones, distinguished according to the number of carbon atoms with their carbonaceous backbone, include monomethyl $(CY_1, n = 0)$, trimethyl $(CY_3, n = 1)$, pentamethyl $(CY_5, n = 2)$, and

heptamethyl (CY_7 , n = 3) (Table 6). CY offers several advantages for the synthesis of phloroglucinol dyes: (1) a narrow spectrum and robust signal; (2) a molar absorption coefficient surpassing that of other fluorescent dyes; (3) easy dissolution in water and low toxicity to tissues and cells, making it suitable for plant bioimaging experiments; and (4) a fluorescence band with enhanced tissue transmittance in the NIR region. 114

Effective methods for analyzing plant stress responses, hazardous substances, and environmental conditions are crucial. In 2022, the N-benzyloxycarbonyl-based Cy-CO2Bz (chemosensor 44) exhibited a strong fluorescence response to NaCl, serving as a sensitive indicator for discerning salt stress within live root tips and whole plants (Fig. 16a). 102 NaCl induced the assembly of N-benzyloxycarbonyl Cy-CO2Bz into a J-aggregate with absorption at 890 nm. This fluorescence response implied its potential as a chemosensor for tracing salt stress in plants. The construction of J-aggregates induced by NaCl implies that it can sensitively and selectively monitor the presence of NaCl. Thus, more J-aggregates should be constructed or more functions of this system discovered for effectively monitoring other indicators to manage the health and living environment of plants. Additionally, the novel π -conjugated indolium salt fluorescent chemosensor 45 based on cyanine derivatives could detect CN in real water samples. With an increase in the concentration of CN, the fluorescence intensity of 45 was enhanced with an LOD of 0.54 nM. The combination 45 with gel- or paper-based indicators showed sensitivity to 1 μM of CN⁻, which could be observed by the naked eye, implying that this chemosensor is a useful tool for monitoring the changes in CN in the living environment of plants (Fig. 16b). Real-time detection of chemical warfare agents (CWAs) in irrigation water and soil can mitigate their threatening effects on plant growth and development. 103 A reversible, colorimetric, and fluorescent sensor for the detection of phosgene based on the cyanine scaffold (chemosensor 46) in an aqueous system was synthesized (Fig. 16c). 104 The rapid dual response of 46 was constructively employed for monitoring phosgene in the environment through strip tests and soil analysis, providing up to ppb (LOD of 0.08 ppb) level detection with distinct color and fluorescence. The NIR fluorescence response of 46 indicated that it has high potential for in vivo imaging owing to its strong tissue penetration and low background interference.

For the detection of pesticides, NIR fluorescent chemosensor 47 was developed, utilizing a cyanine scaffold to generically endorse intrinsic NIR fluorescence and circumventing interference arising from bioluminescence changes (Fig. 16d). 105 An intriguing structural transformation occurs during the sensing event in this protocol, causing a reduction in conjugation. This results in a striking fluorescence change from the near-infrared (816 nm) to the red (637 nm) region, facilitating the proposed ratiometric assay. This receptor also demonstrated capability in monitoring dichlorvos (DDVP) residue in food samples with superior sensitivity and precision, showing potential as a viable substitution for detecting pesticide pollution. Collectively, the literature analysis reflects the universal utility of cyanine derivatives in detecting plant physiological stress responses, ions, and pesticides.

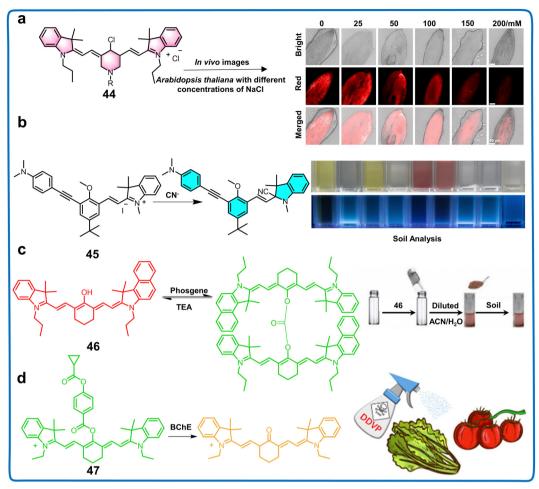


Fig. 16 Structure, mechanism and application of fluorescent chemosensors 44-47 based on cyanine derivatives in live plant imaging, water, soil samples and food. (a) Fluorescent chemosensor 44 for monitoring salt stress of plants. 102 Copyright © 2020, Wiley. (b) Fluorescent chemosensor 45 for monitoring CN⁻ in water. ¹⁰³ Copyright © 2017, Elsevier. (c) Fluorescent chemosensor **46** for monitoring phosgene in soil. ¹⁰⁴ Copyright © 2022, Elsevier. (d) Fluorescent chemosensor 47 for the determination of BChE and detection of DDVP residues in food samples. 105 Copyright © 2023, Elsevier.

Cyanine derivatives have some advantages including favorable molar absorption coefficient, low background interference, high specificity and sensitivity. Alternatively, the defects of these chemosensors mainly include low photostability and aggregation quenching. Therefore, their structure should be modified or the aggregation quenching mechanism exploited to expand the application of cyanine derivatives in plants.

Chemosensors with AIE property

The phenomenon of aggregation-induced emission (AIE) arises due to the restraint of molecular rotations involving rotatable entities such as the phenyl moiety. 115 The low-frequency transitions of rotor-bearing fluorophores in dilute solutions result in weak emission within their excited states. 116 Conversely, upon aggregation, their rotations are obstructed by intermolecular steric interactions, thereby facilitating radiative pathways.¹¹⁷ Unlike traditional fluorophores that succumb to aggregationinduced quenching, AIE emits high levels of light persistently, demonstrating remarkable resilience under challenging bioimaging circumstances prevalent within plant cells. 118

Fluorescent chemosensors with AIE property have been used to analyze the subcellular events of plants because of their superior S/N ratios, intense fluorescence levels and fluorescent stability. In 2017, an AIE based chemosensor (48) was synthesized using diphenylimidazole-In (DPI-In) and saponin (Fig. 17a). 106 48 could specifically label lignin in plant roots with specific "turn-on" emission properties due to its hydrophobicity. This property was effectively utilized to monitor the composition of lignin and morphological modifications that occur during plant growth and developmental stages. Meanwhile, 48 distinguished the meristematic zone in root tissue and primary xylem in stem tissue. Compared with other commercial dyes, 48 showed greater photostability and higher sensitivity, which inspired the modification of the AIE property to manage plant health by bioimaging. In 2023, an AIE-active chemosensor (49) featuring NIR emission was developed, which was capable of four-dimensional spatiotemporal imaging of the morphological changes in plant cell plasma membranes on the subcellular level (Fig. 17b). 107 49 was designed based on the principles of similarity and intermiscibility, a robust imperviousness strategy, and intense electrostatic

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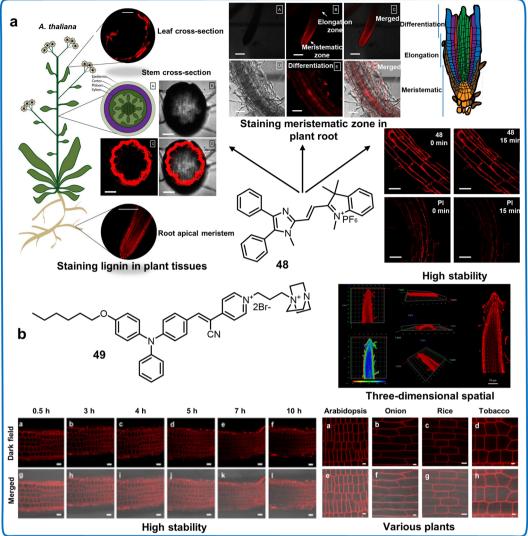


Fig. 17 Fluorescent chemosensors with AIE property for imaging subcellular events in plants. (a) Fluorescent chemosensor 48 monitoring concentration of lignin in root and distinguishing the meristematic zone in root tissue and primary xylem in stem tissue. (b) Fluorescent chemosensor 49 monitoring the morphological and structural alterations of plasma membranes of plant. (c) 2023, The Royal Society of Chemistry.

interactions, making it capable of selectively adhering to plant membranes across diverse plant cell types and plant species. **49** could quickly penetrate the cell wall and stain the cell membrane for up to 10 h and image its integrity. This makes it a highly useful tool for visually tracking plasma membrane-related events in an intuitive and real-time manner. Meanwhile, the favorable imaging performance of **49** for different plant cells indicated that it can be employed to monitor the physiological processes of plasma membranes in different plant species and cell types. We hope that more chemosensors with AIE property be designed to perform more unique and original research into plant bioluminescence imaging.

In summary, modifying the fluorophore modifiable sites in the original series of ancient dyes has revitalized this dye class, offering versatile structures, unique properties and biocompatibility, which have been widely used for imaging plants. Fluorescent chemosensors mainly developed based on the collaborative efforts between chemists and biologists have led to breakthrough progress in developing fluorescent chemosensors, particularly NIR fluorescent ones, despite ongoing challenges, as follows: (i) the majority of NIR chemosensors exhibit limited stability and low QY, making them less suitable for precise and sensitive biological imaging. (ii) Compared to chemosensors with short-wavelength emission, their NIR counterparts often have larger molecular structures, potentially compromising their water solubility. Therefore, the imperative task is to develop small molecular structure NIR dyes and chemosensors with high QY and biocompatibility. Novel heteroatom substitution strategies may represent the most viable approach for constructing these NIR dyes. (iii) To avoid interference from the plant background, it is a necessary to develop NIR-II fluorescent chemosensors or improve their QY. Equipped

with potent fluorophores for investigating the intricate aspects of hazardous substances, plant physiology, adaptation mechanisms, and responses to environmental stimuli, innovative chemosensors will promote advancements in both plant science

4. Applications of fluorescent nano-chemosensors

Nano-based fluorescent chemosensors exhibit great potential in monitoring the health and living environment of plants because of their enhanced surface activity, excellent recyclability, considerable surface area, robust adsorptive capability, outstanding catalytic proficiency, and substantial QY.33,119 Nanosensors are used to detect the presence of chemical species on the nanoscale, which are combined with a fluorophore to significantly enhance their fluorescence efficiency and broaden their range of applications.³³ To date, various nanomaterials including quantum dots (QDs), metal organic frameworks (MOFs), covalent organic frameworks (COFs) and nanoclusters (NCs) have been used to design chemosensors to detect plant components implying plant health and environmental pollutants. 13 In the following sections, we elaborate the applications of various types of nano-based fluorescent chemosensors in monitoring the health and living environment of plants.

4.1 Quantum dots

Review Article

and agricultural research.

Quantum dots (QDs), which are comprised of a group of nanocrystals, exhibit stable photoluminescence (PL), tunable optical properties, and good light stability. Recently, the exceptional optical properties and biocompatibility of QDs have facilitated their use as fluorescent chemosensors for the accurate identification of substances such as hormones, proteins, harmful heavy metals, anions, and pesticide residues, which can imply plant health (Table 7).120 Various types of QDs including semiconductor QDs, carbon quantum dots (CQDs), graphene quantum dots (GQDs), silicon quantum dots (SiQDs), sulfur quantum dots (S QDs), molybdenum disulfide quantum dots (MoS₂ QDs), and MXene QDs are widely used in the detection of these substances. 121 Due to the effectiveness of chemosensor-based QDs in monitoring the health and living environment of plants, we analyze their applications in detail (Fig. 18).

4.1.1 Semiconductor quantum dots. Semiconductor QD chemosensors are mainly composed of semiconductor nanocrystals of group II-VI, IV-VI and III-V, which mainly include CdSe QDs, CdTe QDs, CdS QDs, ZnS QDs, and perovskite QDs. 190 Since 1980, they have gradually become an important tool for replacing organic dyes because of their excellent optical and physicochemical properties. They have been extensively employed for detecting various proteins, hormones and metal ions in plants.

CdSe quantum dots. Among the various semiconductor QDs, CdSe QD chemosensors have been widely used to monitor plant components and irrigation water quality. For the first time, a

CdSe QD fluorescent chemosensor (50) was used to label γ aminobutyric acid (GABA) in plants, and thus determine its distribution in plant protoplasts. 122 Furthermore, its emission efficiency was improved by conjugating a ZnS shell layer to the surface of the CdSe core QD. Due to the increase in the size of the CdSe core QD, its emission peaks were red-shifted (5-20 nm). 50 penetrated and adhered to the cell membrane and specifically bind to the GABA binding pocket on the surface of plant protoplasts, dramatically reducing the fluorescence intensity of the chemosensor. This medium type of chemosensor labeling of GABA in plants provided strong evidence for the presence of the binding site of metabotropic (GABAb) at plant cell membrane (Fig. 19a). 122 Meanwhile, 50 exhibited substantial biological capability in regulating Ca²⁺ signaling within the cell by preventing GABA from permeating the cell, which indicated that it has high potential for regulating plant development and protecting plants from stresses. A thioureaencapsulated CdSe QD chemosensor (51) was prepared through an aqueous photochemical approach utilizing 300 nm UV light in a solution containing acetone, sodium selenosulfate, etc., which could detect the concentration of Hg²⁺ in water. The PL efficiency of this chemosensor decreased with an increase in temperature and pH. Among the many toxic metal ions, only Cu²⁺, Cd²⁺, and Hg²⁺ could significantly quench the fluorescence intensity of the chemosensor, with the LODs of 27.6 µM, 196.0 μM, and 279.2 μM, respectively (Fig. 19b). 123 51 could distinguish various oxidation states of metal ions such as Hg and Cr owing to the photochemically mediated electron transfer between the QDs and metal ions, which implied that 51 can analyze environmental conditions by monitoring the oxidation state of metals. The fluorescent CdSe QD (chemosensor 52) prepared using RNA via a bottom-up method could also be used to detect Hg²⁺ in water, whereas it has characteristics of fluorescence quenching. 124 Therefore, CdSe QD chemosensors show low selectivity and fluorescence intensity in the detection of metal ions, which can be improved by eliminating the interference from the sample matrix and light scattering.

CdTe quantum dots. CdTe QDs, which are water-soluble sulfhydryl-capped QDs, have a narrower emission band in the NIR region than CdSe QDs, making them attractive materials for detecting plant metabolites and water quality for plant survival. A ratiometric QD-based fluorescent chemosensor (53) was recently reported to monitor the distribution and concentration of glucose in plants. 53 was designed based on CdTe/CdS QDs capped with boronic acid (BA)-coupled QDs (BA-QDs) as sensing modules. Upon the addition of glucose, it could catalyze the aggregation of 53 utilizing the covalent bonding between BA and two pairs of cis-diols from glucose. It exhibited impressive fluorescence intensity between 500 and 600 nm, which could monitor the glucose levels in individual chloroplast organelles of A. thaliana. 53 exhibited good sensitivity for glucose detection in plants, and the portable QD glucose sensing method has immense promise to be utilized for the study of photosynthesis and energy transformation in non-model plant species (Fig. 20a). 125 The ability of GSHmodified CdTe QDs (chemosensor 54) to monitor Cu2+ in water

Table 7 Application of QD-based chemosensors in monitoring the health and environment of plants

QD probe types Chemosensors Name	Chemosensors	Name	$\lambda_{ m ex}/\lambda_{ m em}$ (nm)	Linear range	Limit of detection (LOD)	Target analytes	Applications	Ref.
Semiconductor ODs	50	CdSe QDs		1.0×10^{-6} -1.0 × 10^{-3} M	1	γ -Aminobutyric acid	Label of gamma-aminobutyric acid in plant protoplasts	122
	51	CdSe QDs	I	: :	27.6 μΜ 196 μΜ	Cu^{2^+} Cr^{6^+}	Detection of Cu ²⁺ in water Detection of Cr ⁶⁺ in water	123
	52	CdSe QDs	430/585	1	279 μM 1.00 nM	Hg ²⁺	Detection of Hg^{2+} in water Detection of Hg^{2+} in water	124
	53	BA-QD/TGA-QD		500–1000 μM	500 µM	Glucose	Detecting the distribution and concentration of glucose in	125
	54	GSH-CdTe QDs	365/575	20-1100 nM	10.1 nM	Cu^{2+}	plant teat tissue (<i>A. tnatiana</i>) Detection of Cu ²⁺ in water	126
	55	CdTe/ZnS		1	$1.00\times10^{-12}~\mathrm{M}$	Hg^{2+}	Detection of Hg^{2+} in water	127
	26	сdте QDs	390/530	$0.01-1.00 \; \mathrm{\mu g \; mL^{-1}}$	$0.008~{ m \mu g}~{ m mL}^{-1}$	Cr(v1)	Detection of Cr(v1) in water	128
	57	CdTe QDs	589/611	15-80 µM	10.4 nM	CN ⁻	Detection of CN ⁻ in cassava, lake, river water	129
	59	CdTe ODs	450/320	$0.1 \text{ IIM}^{-10} \text{ µM}$ $0-10^{-3} \text{ M}$	$3.40 \times 10^{-8} \mathrm{M}$	Cilioi pyriios Acetaminrid	Montoting the chiotpyinos residue in appies Detection of acetamiprid in water	131
	09	CdTe QDs	400/600	4.49–896 nM	4.49 nM	Dichlorvos (DDVP)	Detecting the dichlorvos (DDVP) residue in apple	132
	61	cds QDs	365/505	1.0–90 ng mL ⁻¹ 8 0–30 ng mL ⁻¹	0.220 ng mL^{-1}	$\operatorname{Cu}^{2+}_{\mathrm{Ho}^{2+}}$	Detection of Cu ²⁺ in laker Detection of Ho ²⁺ in laker	133
				$6.0-90 \text{ ng mL}^{-1}$	1.60 ng mL^{-1}	${ m Mg}^{2+}$	Detection of Mg ²⁺ in laker	
	62	L-Cy-CdS QDs	380/475	$0.05-5 \text{ ng mL}^{-1}$	$39.0~\mathrm{ng~mL}^{-1}$	rinitrophenol	Detection of 2,4,6-trinitrophenol (TNP) in water	134
	63	cds QDs	390/600	I	49.8 μM	(INF) Glufosinate-	Detection of Glufosinate-ammonium in water	135
	64	CIS@ZnS ODs	430/600	I	Mr 00500	ammonium Cu ²⁺	Detection of Cu ²⁺ in water	136
	5		000		5.00 nM	Hg^{2+}	Detection of Hg ²⁺ in water	
	65	Mn:ZnS QDs	310/450	0.19-0.95 μM	0.0200 µM	Methyl parathion	Detection of methyl parathion (MP) in laker, apple	137
	99	ZnS:Mn ²⁺ QDs	1	50 nM-2.5 μM	25.0 nM	(MP) Thiram	Detection of thiram in apple	138
	67	Cs ₃ Bi ₂ Br ₉ :Eu ³⁺ Pe QDs CsPhBr ₂ @CTAB POD	446/620 370/436	5 nM-3 μM 5-100 μM	10.0 nM 30.3 nM	Cu ²⁺ Pendimethalin	Detection of Cu ²⁺ in water Monitoring the concentration of nendimethalin in notatoes	139
	3						and apples	
-	69	$\widetilde{\text{MIP}}$ \otimes $CsPbBr_3QD$	6	$50-400 \text{ ng mL}^{-1}$	$18.8~\mathrm{ng~mL}^{-1}$	Omethoate (OMT)	Detection of omethoate (OMT) in vegetables and soil	141
Carbon QDs	1	CDs	320/388	I	0	V. malı G. 2+	Detecting the infection of V. mall in plants	142
	7.1	CDs	305/400		0.375 nM 5 05 uM	Cu ² .	Detection of Cu ² in union roots Detection of Dh ²⁺ in union	143
	73	Fe_2O_4/CDs	360/435	0.003-0.01 µM	9.300 nM	19	Detection of Ho ²⁺ in water	145
	74	MAB-CDs	280/398	0.5 µM-10 mM	0.100 µM	N_1^{2+}	Detection of Ni ²⁺ in water	146
	75	CDs	610/670	0-70 µM	15.0 nM	Cd^{2+}	Detection of Cd ²⁺ in water	147
	92	CQDs	340/412	5-100 ppb	0.0860 ppb	Arsenite	Detection of arsenite in water	
	77	CDs	320/420	0.01–1.0 µg mL	3.00 ng mL	Chlorpyritos	Detecting the concentration of chlorpyritos on cabbage leaves	s 149
	79	CDs	348/433	$1.0 imes 10^{-10}$ –	$4.80 imes 10^{-11} \mathrm{M}$	Methyl parathion	Detecting the concentration of methyl parathion in cabbage	
	08	ر ا	325/450	$1.0\times 10^{-4}~\mathrm{M}$	$0.050~{\rm ng}~{\rm m}{\rm I}^{-1}$	Diazinon	Detertion of dissinon in tomotose	7. C.7.
	81 81	Tb-CDs	360/463	0.5–15 uM	50.0 nM	ppGpp	Detection of diagnition in contactes Monitoring the concentration of ppGpp in plant	153
	82	MnO_2CD	340/425	0-100 nM	5.75 nM	Arsenic	Detection of arsenic in water and emerald plants	154
	83	NCDs	370/450	0.01–1 μM 0.001–1 μM	4.80 nM	Hg ²⁺	Detection of Hg^{2+} in water Detection of Ao^+ in water	155
	84	s-cqds	360/435	25-250 µM	0.960 мм	Fe ³⁺	Detection of Fe ³⁺ in water	156
	85	N-CDs		$11.24-241~{ m \mu g}~{ m L}^{-1}$	$7.45 \mathrm{\mu g L^{-1}}$	Cd^{2^+}	Detection of Cd ²⁺ in lake	157
	85 87	N, S-CQDs	350/450	$\frac{-}{0.3-1000}$ Hg 1^{-1}	500 ppb 30.0 ng L^{-1}	Carbaryl Organophosphorus	Monitoring the carbaryl residue in apples Detection of organophosphorus pesticides in soil	158
	;			0.1	0-			

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QD probe types	Chemosensors Name	Name	المال	Limit of detection (LOD)	Target analytes	Applications	Ref.
	88	N-CD-Fla	400/502 1.0-2000 nM	0.36 nM	Fenitrothion	Monitoring the concentration of fenitrothion in rice	160
	68	N-CDs		3.00 pM	Atrazine	Monitoring the concentration of atrazine in cucumbers	161
	06	N-CDs		$3.50~{\rm \mu g~L^{-1}}$	Methiocarb	Monitoring the concentration of methiocarb in cabbage	162
	91	N-CDs	$370/450~0-5 imes 10^{-4}~\mathrm{M}$	$1.00\times10^{-7}\mathrm{M}$	p-Nitroaniline	Detection of <i>p</i> -nitroaniline in soil and water	163
	92	NCQDs@Co-		$0.350~\mathrm{ng~mL}^{-1}$	Jasmonic acid (JA)	Monitoring the distribution and concentration changes of	164
,		MOFs@MIPs			ē	Jasmonic acid (JA) in plant	
Graphene QDs	93	GQDs	320/440 —	1.17 µM	Hg_+	Detection of Hg ⁻⁷ in water	165
				2.46 µM	Cd	Detection of Cd ⁻ in water f	
	70	DELCODE	390/460 0-1 M	2.01 µM	FD F9 ²⁺	Monitoring the concentration of PD in water Detection of Eo^{2+} in unter	166
	1.	rErdQDs			Cu ²⁺	Detection of Cu ²⁺ in water	100
	50	GODs	300/456 9 9-435 0 nM	Mu 009 0	Dh ²⁺	Detection of Dh^{2+} in water	167
	96	GODS/AmNPs		0.520 IIM	Z Z	Monitoring the distribution of CN in plant	168
	65	B-/N-GOD	320/425 —	0.00620 mo L ⁻¹	Paradilat	Detection of paradulat in water	169
	86	N-GODs	320/423 0.1–17 nM	0.041 pM	Omethoate	Detection of omethoate in cabbace leaves and water	170
	66	GODS-AONDS		9.00 no mL ⁻¹	Glynhosate	Monitoring the glyphosate residue in peas	171
	100	GODS/ACPE/CHOV	362/467 0 1-10 mm	0.172 mm	Dichloryos	Detection of dichloroos in the lake	172
Silicon ODs	101	Si ODs		0.430 uM	Chlorogenic acid	Monitoring the concentration changes of chlorogenic acid	173
	}				(CGA)	(CGA) in plant	
	102	S-SiQDs	345/425 1-20 µM	0.210 µM	Fe^{3+}	Detection of Fe ³⁺ in water	174
	103	N-SiQDs	_	24.0 nM	Hg^{2+}	Detection of Hg ²⁺ in water	175
	104	Si QDs-AuNPs-CdTe	_	16.3 nM	Carbaryl	Detection of carbaryl in water, soil, and cabbage	176
		ÓDs					
Molybdenum	105	Eu-MoS ₂ QDs		23.8 µM	ppGpp	Detection of ppGpp in plant	
disultide QDs	106	$MoS_2QDs-MnO_2$	360/430 0.33-5.00 µМ	39.0 nM	Ascorbic acid	Monitoring the distribution of ascorbic acid in hawthorn and	1/8
	107	MoS,ODs	$360/440 \ 3.3 \times 10^{-7}$	50.0 uM	Pb^{2+}	Led dates Detection of Pb ²⁺ in water	179
				-			
	108	$B-MoS_2QDs$	_	1.80 nM	$^{+}$ g ²⁺	Detection of Hg ²⁺ in lake water	180
	109	β -CD-MoS ₂ QDs	289/400 0.01-18.0 ppm	3.30 ppb	Parathion-methyl	Detection of parathion-methyl (MP) in water	181
Sulfur ODe	110	SODs	320/431 5_50 uM	7 51 uM	(MP)	Monitoring the concentration of Co^{2+} in roots and stams of	183
say ining	011	2452	•	4.5 t puvi	3	Salvia miltiorrhiza	707
	111	Apt-SODs	$- 10^{-15} - 10^{-7} \mathrm{M}$	0.300 fM	Hg^{2^+}	Detection of Hg ²⁺ in laker, river	183
	112	r-SDs	$360/440 1.0-50.0 \ \mu mol \ L^{-1}$		Cu ²⁺	Detection of Cu ²⁺ in laker	
	113	RhB-SQDs	455/580 0.050-	17.3 ng mL^{-1}	2,4-	Detection of 2,4-dichlorophenoxyac etic acid (2,4-D) in water	
			$0.500~\mathrm{\mu g~mL}^{-1}$		Dichlorophenoxyac		
ACV COLO	7			94.00	etic acid $(2,4-D)$	Potentian of Ma(-) in Island Investigate	707
MAERIE QUS	114	Ti-C-ODs	350/442 0-1./ µM 380/470 —	30.0 mM	$\frac{\mathbf{M}\mathbf{n}(\mathbf{v}\mathbf{n})}{\mathbf{C}\mathbf{r}^{3+}}$	Detection of Mil(VII) III taker, piant reaves Detection of Cr ³⁺ in water	180
	116	N-Ti,C, MXene ODs	330/453 0-2000 uM	10.0 uM	Cu^{2^+}	Detection of Cu ²⁺ in water	188
	117	N-MQDs	_	1.21 µM	Alizarin red (ARS)	Detection of alizarin red (ARS) in water	189
	118	$UA@Ti_3C_2QDs$	360/420 0.01-40 μM	9.58 nM	2,4,6-Trinitrophenol	Detection of 2,4,6-trinitrophenol in water	189

Table 7 (continued)

Wines Carbon Que Graphene QDs Probe

Control Cd2+

Pb2+

Cu2+

Mos Que Sulfur QDs

Sulfur QDs

Silicon Que Silicon

Fig. 18 Application of quantum dot-based fluorescent chemosensors for monitoring the living environment and elements of plants.

Plant hormone detection

was recently reported. When the excitation wavelength was 365 nm, a fluorescence emission peak appeared at 575 nm. The QY of the chemosensor markedly diminished with an increase in the concentration of Cu²⁺. An excellent correlation was observed between Cu2+ concentration and the fluorescence decay of 54, spanning the concentration range of 20 to 1100 nM with an LOD of 10.56 nM (Fig. 20b). 126 Also, it was successfully used for the detection of Cu2+ in lake water and plants, which has great potential for monitoring food safety and water quality. Some heavy metals such as Hg^{2+} and Cr^{6+} were also detected by CdTe QD chemosensors (55 and 56).127,128 55 was comprised of MSAfunctionalized CdTe/ZnS core/shell (CS) QDs, which showed high selectivity for monitoring Hg²⁺ by electron transfer. To promote the application of 55 in the detection of water quality, a preliminary electronic apparatus should be established. The GSH capping layer of 56 can bind with Cr⁶⁺, realizing the detection of different ions by changing the crystallite dimensions of QDs. This strategy makes it easy to obtain QDs chemosensors. For instance, N-acetyl-L-Cys (NALC) CdTe QDs (chemosensor 57) could also be synergized with carbon dots (CDs) for the detection of CN-. 57 exhibited unique absorbance and emittance wavelengths at 589 nm and 611 nm, respectively. CDs and CdTe QDs showed bright blue and red colors under UV light, respectively. The fluorescence from 57 was first quenched by the introduction of Cu²⁺, while the fluorescence of 57 significantly recovered upon the addition of CN-. Ultra-LODs as low as 10.35 nM were achieved for CN- concentrations in cassava and water samples in the range of 0.02-10 µM and 15-80 µM,

respectively (Fig. 20c). 129 This ratiometric chemosensor could realize the highly sensitivity detection of CN at the nM level and accurately determine its concentration in real samples. In addition, a CdTe OD chemosensor (58) was developed to detect the residue levels of organophosphorus pesticides in apples. The surface coordination of thiourea in the basal medium strongly inhibited the green emission of 58 through the FRET mechanism, and its fluorescence was gradually restored upon the addition of chlorpyrifos. The fluorescence of 58 was linear at concentrations in the range of 0.1 nM to 10 µM with an LOD of 0.1 nM for apples (Fig. 20d). Based on this type of chemosensor, it was also possible to realize the accurate detection of anilinophos and dichlorvos in water (chemosensor 59 and 60, respectively). 131,132 The detection mechanism of 60 was based on the inhibition of enzymatic activity (AchE) but the stability of AchE may limit its application in practice. This phenomenon indicates that an automatic biochemical analyzer should be developed for combination with 60. CdTe QD chemosensors have been widely used in detecting water pollution but improving their detection performance remains a challenge.

CdS quantum dots. CdS QDs have unique optical and electronic properties such as high fluorescent emission and light bleaching resistance, which can be used to monitor the quality of irrigation water. For example, a yellow fluorescent CdS QD chemosensor (61) was reported for the detection of Cu^{2+} , Hg^{2+} , and Mg^{2+} in water samples. The peak values for the excitation

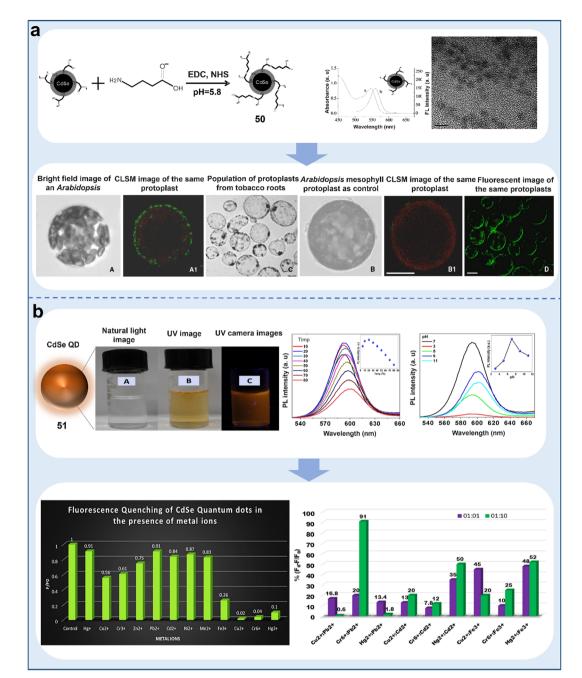


Fig. 19 Schematic representation of CdSe QD-based chemosensors for the visualization of plant protein level and ions in water. (a) Specific recognition and detection of GABA on the surface of plant protoplasts based on ZnS outer shell layer and CdSe inner core QD. 122 Copyright © 2006, Elsevier. (b) Detection of heavy metal Hg²⁺ in water based on starch-capped CdSe QDs. ¹²³ Copyright © 2020, Elsevier.

and emission wavelengths of 61 were recorded to be 365 nm and 505 nm, respectively, and the color under UV irradiation was an intense yellow. **61** could be linearly quenched by Cu²⁺, Hg^{2+} , and Mg^{2+} in aqueous solution with LODs of 0.22, 5.8 and 1.6 ng mL⁻¹, respectively (Fig. 21a). ¹³³ In the presence of GSH, the fluorescence intensity of 61 increased 1.5-fold, which implied that 61 can be used to monitor the stress damage caused by ions in plants. The ability of L-Cys-coated cadmium sulfide QDs (L-Cys-CdS QDs) (chemosensor 62) with strong fluorescence was reported to detect 2,4,6-trinitrophenol (TNP) in environmental water samples. Particularly, the PL emission peak of 62 remained unaffected by a change in the excitation wavelength. The emission spectrum was strongest upon excitation at the wavelength of 365 nm. It was highly selective for TNP, and an apparent reduction in fluorescence intensity of CdS QDs was observed with an increase in TNP concentration, and its quenching effect was better under weakly acidic conditions. The linear range of TNP concentration was determined to be $0.05-5 \mu g \text{ mL}^{-1}$ with the LOD of 39 ng mL⁻¹ (Fig. 21b). 134 Furthermore, a program for the accurate, discerning detection

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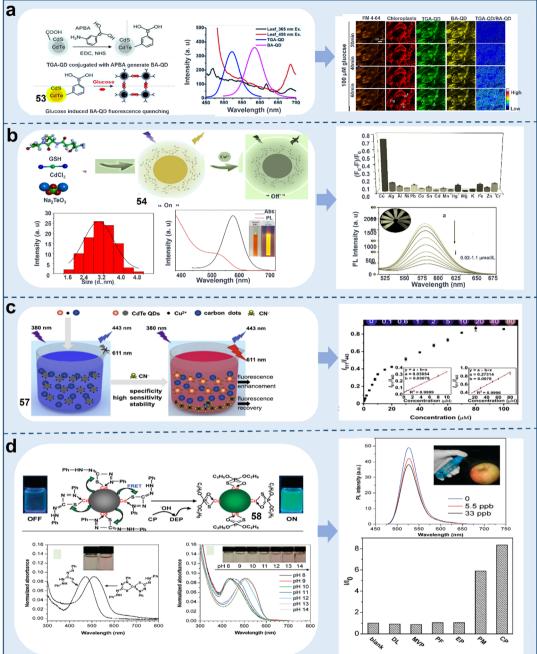


Fig. 20 Schematic representation of CdTe quantum dot-based chemosensors for detecting ions and pesticides in plants and water. (a) Ratiometric fluorescent chemosensors based on TGA-QD and BA-QD for monitoring the glucose content in plant chloroplast organelles. 125 Copyright © 2018, the American Chemical Society. (b) Detection of heavy metal Cu²⁺ in environmental water samples by glutathione-modified CdTe QD. 126 Copyright © 2023, Elsevier. (c) Detection of cyanide anions based on synergistic interaction of N-acetyl-L-Cys-capped CdTe QDs and CDs. 129 Copyright © 2019, Elsevier. (d) Detection of the organophosphorus pesticide chlorpyrifos in apples based on CdTe QD fluorescent chemosensor. 130 Copyright © 2010, the American Chemical Society.

methodology for quantifying trace levels of TNP in water was developed. In addition, the CdS QD chemosensor (63) also enabled the accurate monitoring of dichlorvos (DDVP), paraquat, and glufosinate in environmental water samples with LODs of 0.23 mM, 1.44 μ M and 49.8 μ M, respectively. ¹³⁵ Paraquat possesses the capacity to quench the fluorescence of QDs, DDVP significantly enhances their fluorescent intensity, and glufosinate induces a blue-shift and increase in fluorescence intensity. Based on these results, we can develop software for use with a smartphone to realize the fast detection of various pesticides in the environment. Future studies should focus on improving the biocompatibility of CdS QD chemosensors to expand their imaging in plant tissues.

ZnS quantum dots. Compared with other semiconductor quantum dots, ZnS QDs are more stable, non-toxic, and ecologically safe, and thus widely used in biosensing and toxic

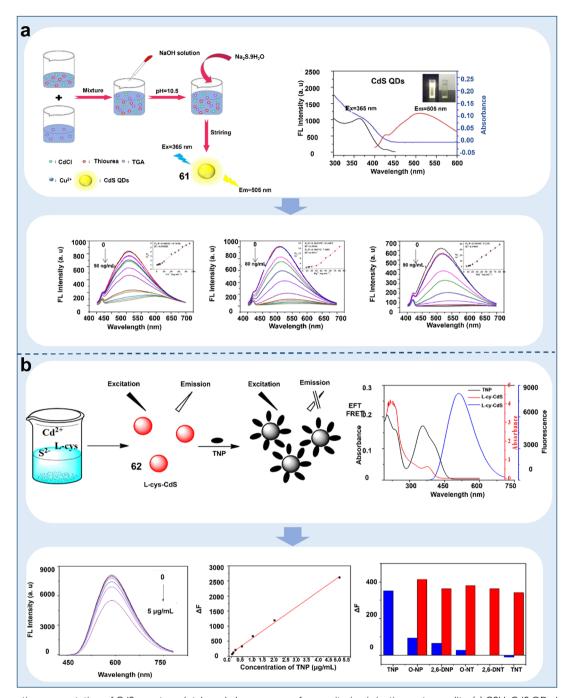


Fig. 21 Schematic representation of CdS quantum dot-based chemosensors for monitoring irrigation water quality. (a) GSH-CdS QD chemosensor for the accurate detection of Cu²⁺, Hg²⁺, and Mg²⁺ in water.¹³³ Copyright © 2022, Elsevier. (b) Detection of TNP in environmental water samples based on L-cysteine-coated cadmium sulfide quantum dot chemosensor. 134 Copyright © 2019, Elsevier.

substance detection technologies. 191 For example, CuInS2@ZnS (CIS@ZnS) (chemosensor 64) core-shell QDs were reported for the sensitive detection of heavy metals in water. 64 showed a PL excitation peak at 450 nm and emission peak at 620 nm, and the core-shell QDs exhibited blue shifts with a significant increase in emission intensity. The QY of their PL was 95%. By adding various heavy metals such as Ar³⁺, Cd²⁺, Co²⁺, Cu²⁺, Fe²⁺, Hg²⁺, and Zn²⁺, which are commonly found in water, to aqueous dispersions of 64, it was found that the PL of the chemosensor was quenched by the test metal ions at the nM level, such as Cu²⁺ and Hg²⁺, with an LOD of 0.22 nM in evaluating water quality (Fig. 22a). 136 Besides the detection of ions, 64 could also monitor changes in cholesterol and citric acid, implying its potential as a tool to evaluate fruit quality. A proportional fluorescent chemosensor based on double-emitting Mn-doped ZnS QDs (Mn:ZnS QDs) (chemosensor 65) was demonstrated for the detection of Pb²⁺ and methyl parathion (MP). 65 was designed to show blue fluorescence at 400-500 nm, which was highly sensitive as a proportional fluorescent chemosensor for the

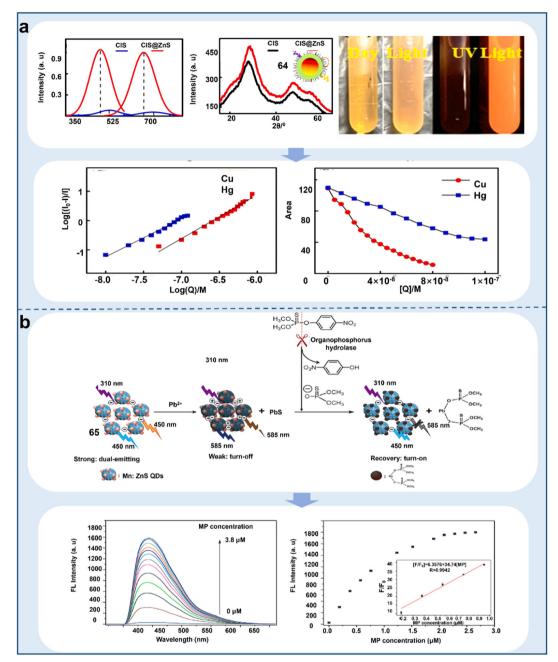


Fig. 22 Schematic representation of ZnS quantum dot-based chemosensors for detecting ions and pesticides in water. (a) Efficient detection of copper and mercury in water quality based on CIS@ZnS QD chemosensor.¹³⁶ Copyright © 2021, Elsevier. (b) Novel proportional fluorescent chemosensor based on luminescent manganese-doped ZnS QD (Mn:ZnS QD) for the detection of Pb²⁺ and methyl parathion (MP).¹³⁷ Copyright © 2019, Elsevier.

detection of Pb2+. This chemosensor showed good concentration linearity between 10 nM and 60 nM for Pb²⁺, with an LOD of 0.5 nM. Also, 65 served as a "turn-on" fluorescent chemosensor for detecting the concentration of MP. The fluorescence response of this chemosensor showed an excellent linear response for MP in the concentration range of 19.0–450.0 μ M, with LOD of 0.02 μ M (Fig. 22b). ¹³⁷ This sensor system was employed to identify MP residues in apples and lake water. Considering the complexity of environmental samples and unknown interferences, a specific response structure or recognition moiety should be combined with 65. In addition, a ZnS QD-based chemosensor (66) also enabled the accurate detection

of thiram in environmental water samples and fruit peels. 138 In the presence of thiram, the Ag+ in 66 could form an Ag-thiram complex, which could suppress the phosphorescence quenching, indicating that a UV lamp can be used to easily realize pesticide detection. Therefore, compared with other semiconductor quantum dots, ZnS has lower toxicity and better stability, which has broader prospects for plant imaging in the future.

Perovskite quantum dots. Perovskite QDs are recently developed semiconductor QDs that have great potential for detecting heavy metals in soil and water. For example, the ability of Eu³⁺-

doped lead-free Cs₃Bi₂Br₉ Pe QDs (chemosensor 67) to detect Cu²⁺ in real water samples on was reported. The UV-vis absorption spectra of 67 and 67:Eu³⁺ showed that the absorption band edge of the bare 67 was at 389 nm. The absorption band shifted towards a higher wavelength with an increase in the concentration of Eu3+. 67:Eu3+ was characterized by high QY, nontoxicity, robust stability and multi-color emissions, thereby conferring heightened sensitivity and selectivity for detecting metal ions in environmental water. Notably, the exciton emission at 446 nm was rapidly perturbed upon the introduction of

Cu²⁺, which has excellent detection efficiency for Cu²⁺ in the concentration range of 5 nM to 3 µM, with an LOD of 10 nM (Fig. 23a). 139 PS-CsPbBr₃ (a) CTAB PQDs (chemosensor 68) acted as a sensor, exhibiting blue fluorescence under UV light. 68 could be used to detect dimethoate in water, and the addition of the pesticide dimethoate resulted in the fluorescence shutdown of 68. Notably, linear quenching was achieved with an increase in the concentration dimethoate in the range of 5-100 μM with an LOD of 5.0 nM. The developed method exhibited higher sensitivity compared with analytical instruments

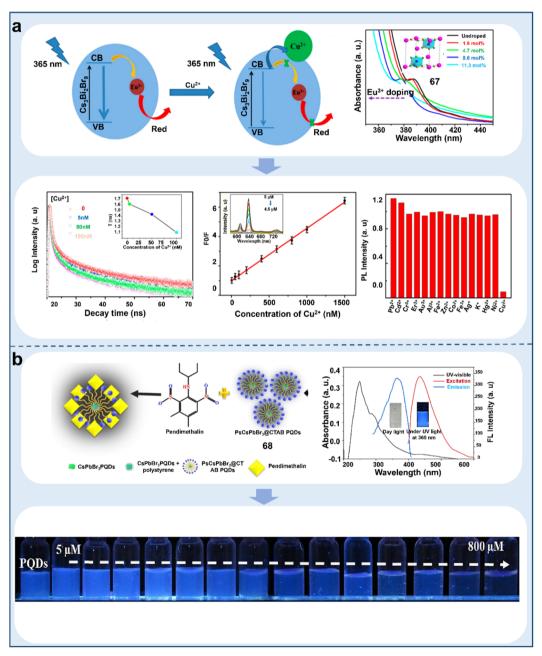


Fig. 23 Schematic representation of chalcogenide-based quantum dot chemosensors for monitoring the concentration of ions and pesticides in water. (a) Eu³⁺-doped lead-free Cs₃Bi₂Br₉ Pe QD fluorescent chemosensor for the detection of Cu²⁺ in real water samples.¹³⁹ Copyright © 2019, the American Chemical Society. (b) Detection of the pesticide dimethoxybenzoate by the introduction of polystyrene and cetyltrimethylammonium bromide as an encapsulated assembly system prepared as CsPbBr₃@CTAB PQD. 140 Copyright © 2019, Elsevier.

(Fig. 23b). 140 In addition, the fluorescent sensor prepared by combining a molecularly imprinted polymer (MIP) with luminescent perovskite (CsPbBr₃) (chemosensor 69) encapsulated in (3-aminopropyl) triethoxysilane (APTES) could sensitively detect oxidized lecithin in soil with an LOD of 18.8 ng mL⁻¹. 141 However, the low water-soluble of perovskite QDs is a challenging task, and thus focusing on improving their stability and water solubility will increase their application scope in the biological field.

Although semiconductor QDs have been widely used to monitor pollutants in the living environment of plants, their application in plant imaging is limited, which is mainly attributed to the following factors: (i) the in vivo imaging technology of semiconductor QDs is constantly improving, but the sensitivity of fluorescence imaging for deep tissues is low; (ii) the inertness of semiconductor QDs in vivo may cause enduring toxicity to organisms; and (iii) semiconductor QDs have high surface activity, which make them easily agglomerate to form larger agglomerates.

4.1.2 Carbon quantum dots. CQDs are novel and green carbon nanoparticles, characterized by particle dimensions generally smaller than 10 nm. CQDs also exhibit interesting fluorescence properties because of their excellent fluorescence properties and physicochemical properties such as good water solubility, low toxicity, and great biocompatibility. 192 Thus, non-doped CQD chemosensors, metal-doped CQD chemosensors and non-metal-doped CQD chemosensors have been used as chemical and biological sensors to achieve the precise detection of substances affecting plant health.

Undoped carbon quantum dots. CQDs are mainly prepared from some natural plants and biomolecules, which are widely used in monitoring fungi, reactive oxygen species, and heavy metals in plants because of their impressive biocompatibility, negligible toxicity and remarkable stability. 193 For example, fluorescent CQDs (chemosensor 70) were designed for the first time for monitoring pH changes in plant cells. 70 exhibited excitation-dependent fluorescence behavior, and its fluorescence emission intensity changed with pH. The gradual increase in fungal concentration in infected apple tissues led to a transient decrease in pH in plant cells, which caused the fluorescence intensity to increase. Consequently, the fluorescence imaging of the pathogenic fungus Valsa mali Miyabe et Yamada in apple tissues was realized (Fig. 24a). 142 Meanwhile, the fluorescence of 70 in dead cells was quickly quenched because of the absence of cellular pH regulation, implying that this chemosensor can be developed into a kit for the visualization of pH regulation in plants or distinguishing live or dead cells. Accurate monitoring of Cu²⁺ in plants could be realized based on fluorescent R-CDs (chemosensor 71). The fluorescent carbon dots were well dispersed and water-soluble. 71 exhibited bright-red emission at 680 nm when excited at 420 nm. The red emission of 71 was found to decay upon interaction with Cu²⁺ in solution by incubating 71 with bean sprouts, and then transferring them to a solution of Cu²⁺. The LOD was 25 nM in plants. 71 was capable of overcoming the influence from the internal environment of the plant and had excellent immunity to interference, implying that this chemosensor can monitor the stress in plants in practice with nondestructive nature (Fig. 24b). 143 Also, the accurate detection of Pb2+, Ni2+, Hg²⁺, Fe³⁺, Cr⁶⁺, and Cd²⁺ in environmental water samples could be realized based on fluorescent CQDs (chemosensor 72-75). 444-147 Among them, 73 showed the lowest detection limit of 0.3 nM, which can effectively coordinate with Fe₃O₄/ CDs by electrostatic interactions, and then quench their fluorescence signal. The results indicated that 73 can not only detect Hg2+ in the actual environment but also remove Hg2+. A CQD chemosensor (76) could detect arsenite in environmental water samples. 76 showed the strongest emission wavelength at 412 nm when excited at 340 nm and its solution appeared blue under UV light. The SH-groups of 76 could selectively interact with arsenite, which enabled the sensitive detection of arsenite in environmental water with a good response in the range of 5-100 ppb and LOD (3 s) of 0.086 ppb (Fig. 24c). However, considering that the excitation wavelength of 76 in the UV region, it is not suitable for in vivo imaging of Hg2+.148 In addition, it was reported that CDs (chemosensor 77) synthesized by burning waste paper as a carbon source could detect chlorpyrifos pesticide in vegetables. The fluorescence spectrum of 77 reached its optimum emission peak at 420 nm with an excitation wavelength of 320 nm. Its fluorescence was quenched by Fe²⁺ and recovered upon the introduction of chlorpyrifos. The linear concentration range extended from 0.01 to 1.0 μg mL⁻¹, featuring an LOD of only 3 ng mL⁻¹, which was used for imaging chlorpyrifos in vegetables (Fig. 24d). The fluorescence of 77 depended on the transformation between Fe2+ and Fe3+ by H2O2 and the production of H₂O₂ was inhibited by acetylcholinesterase activity, implying that this chemosensor can quantitatively detect organophosphorus pesticides and monitor enzymatic activity. 149 In addition, fluorescent chemosensors (78-80) based on CDs also enabled the accurate detection of some pesticides in plants such as parathion-ethyl, cyfluthrin, glyphosate, methomyl and methyl parathion. 150-152 Among them, 79 showed the lowest detection limit of 4.8×10^{-11} M owing to its detection mechanism, where methyl parathion can decrease the enzyme activity of tyrosinase. Therefore, the excellent fluorescence properties based on fluorescent CQDs enable them to be used more often as chemosensors in plants, consequently enabling an in-depth understanding of plant growth conditions and patterns.

Metal-doped carbon quantum dots. In recent years, doping different metal elements is an important way to enhance the physicochemical attributes of CQDs to make them more stable, and they are widely used in sensing applications. For example, Tb³⁺-doped CDs (CD-Tb) (chemosensor 81) showed bright-blue fluorescence emission under a 365 nm UV lamp with a relatively high QY of 54.8%. Subsequently, its sensitivity to guanosine 3'-diphosphate-5'-bisphosphate (ppGpp) was evaluated. The ppGpp molecular phosphate group was found to be able to bind to the rare-earth Tb³⁺, and thus effectively improved the emission intensity of 81. Paper-based sensors were developed to realize simple and intuitive ppGpp detection. A linear

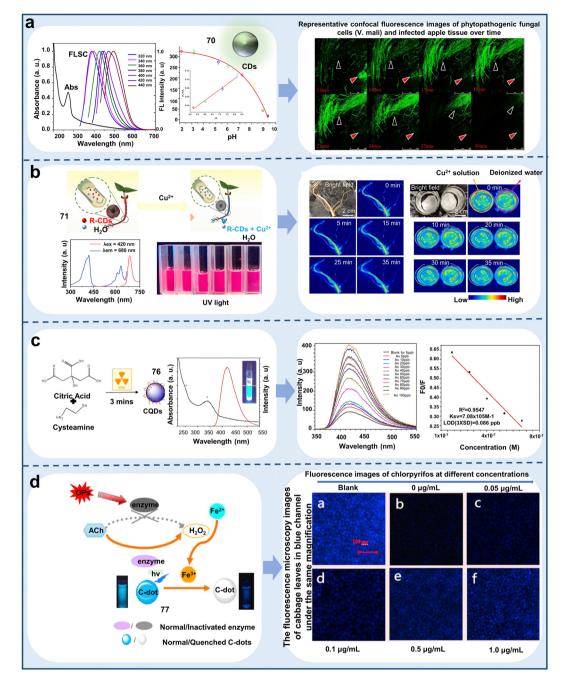


Fig. 24 Schematic representation of the application of undoped carbon quantum dot-based chemosensors for detecting pathogens and water pollution. (a) Hydrothermal preparation of pH-sensitive fluorescent CDs for the detection of the pathogenic bacterium Valsa mali Miyabe et Yamada in apple tissues. 142 Copyright © 2015, Elsevier. (b) Fluorescent sensors of red fluorescent R-CDs enable Cu²⁺ concentration monitoring in plant roots. 143 Copyright © 2014, Elsevier. (c) Fluorescent sensor of blue fluorescent CDs enables the sensitive detection of arsenite in environmental water samples. 148 Copyright © 2017, Elsevier. (d) Detection of chlorpyrifos levels in cabbage leaves by a blue fluorescent CD sensor. 149 Copyright © 2018, Elsevier.

relationship emerged in a broad concentration range of 25 to 750 µM (Fig. 25a). Among the tested amino acids, 81 could selectivity detect ppGpp owing to the production of antenna and coordination binding. 153 This scheme confirmed the great potential of rare earth ion-modified CDs as a novel proportional FL chromophore. An MnO2-doped carbon QD chemosensor (MnO₂CD) (82) was prepared by a hydrothermal methodology based on the combination of citric acid and KMnO₄. This chemosensor exhibited good photostability with no discernible alteration in its PL spectra, even in the presence of elevated NaCl concentrations up to 2.5 M. No change in its PL peak position was observed with a change in pH conditions. Importantly, 82 enabled the first visual identification of arsenic-containing compounds in rice and green plants. The luminescence signal of 82 was mainly presented in the vascular system of the roots, and As³⁺ was linearly correlated in the concentration range of 0-0.991 µM. The LOD of

arsenite in the chlorotic plants reached 9.2 µM (Fig. 25b). 154 Thus, 82 showed good translocation properties in lateral and green rice plants, demonstrating its potential for detecting the deposition of arsenic within plant root structures. The temperature-sensitive fluorescent properties of the chemosensor of MnO₂CD establish its potential for use as a nanotemperature meter in physiological environments. Therefore, the introduction of metal ions increases the detection range of CQDs.

Nonmetal-doped carbon quantum dots. Compared with metal element doping, nonmetal-doped CQD chemosensors with low toxicity, good biocompatibility, and high-intensity PL have been used in biosensing and environmental monitoring. For example, nitrogen-doped carbon QDs (NCDs) (chemosensor 83) prepared using uronic acid were reported to be capable of detecting Hg²⁺ and Ag⁺ in water. 83 exhibited a light transparent color under daylight conditions and a bright-blue color under 365 nm excitation. The fluorescence intensity of 83 could

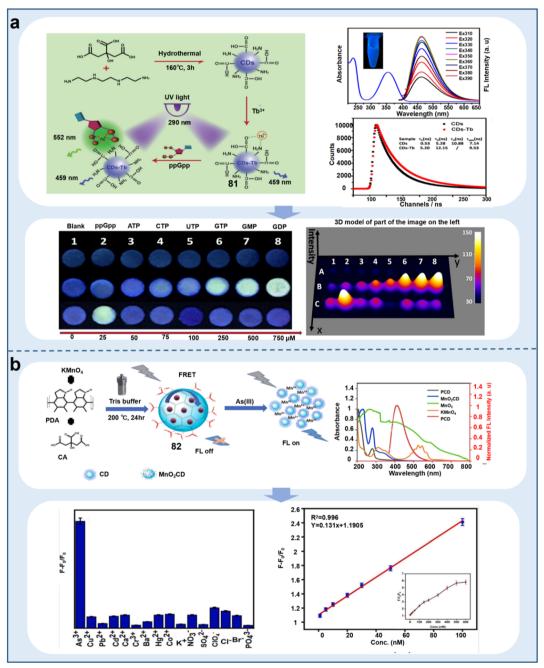


Fig. 25 Schematic representation of metal-doped carbon quantum dot-based chemosensors for monitoring the living environment of plants. (a) Terbium-modified fluorescent CD chemosensor for the detection of ppGpp. 153 Copyright © 2018, the American Chemical Society. (b) Detection of As(III) in environmental water samples by MnO₂ CD fluorescent chemosensor synthesized by hydrothermal decomposition. ¹⁵⁴ Copyright © 2022, Elsevier.

be linearly quenched in the presence of Hg²⁺ and Ag⁺ in water with LODs of 4.8 nM and 1 nM, respectively (Fig. 26a). Furthermore, 83 could be recovered by EDTA solution, indicating that this chemosensor may be a potential tool for sensing Hg²⁺/Ag⁺ in the real environment because of its recyclability. 155 NCD chemosensors enabled accurate detection of Fe³⁺, Pb²⁺, Cr²⁺, and Cu2+ in water (chemosensors 84 and 85). Among them, 85 is an electrochemical sensor that could sensitively

detect Pb2+ and Cr2+ owing to its electroactive surface and oxygen-functional groups. CQDs based on N, S co-doping (N, S-CQDs) (chemosensor 86) also accurately detected carbaryl in apples. 86 achieved a QY of 12.5% with a PL lifetime of 2.8 ns, and carbaryl could quench its fluorescence in the presence of acetylcholinesterase. The linear concentration range was 6.3 imes $10^{-9}\,\mathrm{g\,L^{-1}}$ to $6.3 \times 10^{-4}\,\mathrm{g\,L^{-1}}$, with the lowest detection limit of 5.4×10^{-9} g L⁻¹ because of its dual enzyme response

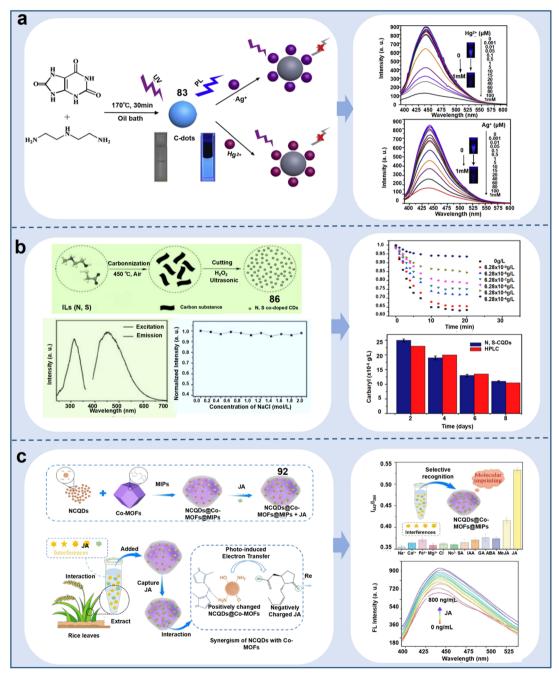


Fig. 26 Schematic representation of non-metal doped carbon quantum dot-based chemosensors for monitoring ions in water, pesticides and hormones in plants. (a) Fluorescent chemosensors with N-doped carbon dots for the detection of Hg²⁺ and Ag⁺ in water samples. ¹⁵⁵ Copyright © 2017, Elsevier. (b) Fluorescent chemosensors of N, S co-doped carbon quantum dots were used for the detection of the pesticide carbaryl in fruit samples. 158 Copyright © 2016, Elsevier. (c) Detection of phytohormone jasmonic acid based on NCQD@Co-MOFs@MIP ratiometric fluorescent chemosensor. 164 Copyright © 2023, Elsevier.

mechanism (AChE and ChOx enzymes) (Fig. 26b). 158 N, S-CQD chemosensors also enabled the fluorescence detection of paraoxon, p-fenitrothion, dithiopyr, aflatoxin, methimazole, and fenitrothion in soil, water or vegetable samples (chemosensors 87-91). Among them, 88 was been proven to detect fenitrothion, dinoseb, dithianon, and their analogues, which was attributed to the electron transition of C=N in flavonoids. Additionally, fluorescent NCDs, metal-organic frameworks, and molecularly imprinted polymers, in conjunction with a proportional fluorescent sensor NCQD@Co-MOFs@MIPs (chemosensor 92), were proposed for the accurate quantification of the jasmonic acid (JA) content in plants. This groundbreaking study represented the first instance integrating fluorescent carbon dots with these composites. Co-MOF and MIPs acted synergistically in trapping the JA molecule, improving the sensitivity and selectivity for monitoring the distribution of JA. Upon the incorporation of JA in 92, it formed a chemical interaction with the NCQDs via PET, leading to changes in the fluorescence signal of 92. The LOD reached 0.35 ng mL⁻¹, offering new insights for developing low-cost and highly sensitive methods for monitoring phytohormones.

Implying that 92 is useful for monitoring the response of plants to biotic and abiotic stresses (Fig. 26c). 164 Therefore, the combination of non-metallic doped quantum dot chemosensors and smartphones and composites is an important approach to improve the detection efficiency and practical applications.

Compared with semiconductor QDs, CQDs have some advantages such as low cytotoxicity, high biocompatibility, and fluorescence stability, but CQDs also have some disadvantages, as follows: (i) the fluorescence wavelength of CQDs is 400-520 nm, and most of them require UV excitation. This short-wavelength has low penetration depth in biological tissues and easily causes photodamage to biological tissue. (ii) Short-wavelength can cause strong autofluorescence in biological tissues, resulting in serious fluorescence background, which interferes with the analysis of fluorescence signals.

4.1.3 Graphene quantum dots. GQD chemosensors, a class of carbon-based QDs, have been used to monitor the water quality for plant survival and non-metal ions in plants. For example, using graphene oxide as a precursor, GQD (Chemosensor 93) was prepared via a simple hydrothermal method for monitoring various heavy metal ions in water. Due to the different functional groups in 93, the particles were different sizes and had surface states, which showed different excitation and emission spectra. In aqueous medium, its fluorescence intensity gradually decreased with an increase in the concentration of Hg²⁺, Cd²⁺ and Pb²⁺ due to the effective energy transfer. Metal ions exhibited a "turn-off" fluorescence response when they were coordinated with the functionalities of 93. The LODs for the three metal ions were 1.171 μ M, 2.455 μ M and 2.011 μ M, respectively, confirming the feasibility of 93 as promising material for the detection of heavy metal ions in water samples (Fig. 27a). However, its same emission wavelength decreased its selectivity for detecting ions, implying that we should introduce attractive or specific sensing units for distinguishing different ions.165 Heavy metals and pesticides in soil or water can also

affect the survival of plants, and GQD chemosensors have also been widely used for the accurate detection of Cu²⁺, Pb²⁺, Fe³⁺, and Cr³⁺ (chemosensors 94 and 95). 166,167 The major component of 94 and 95 was coffee grounds and graphene, respectively, which showed good reproducibility, implying that we can develop opto-electronic devices or photocatalysis to increase their application scope. This type of chemosensor also enabled the real-time monitoring of evanide in plant species. The strategy involved using GQD/gold nanoparticles (AuNPs) coupling to sense and image endogenous bio-cyanide in plants. The GQDs were assembled on the surface of AuNPs by π - π stacking of the GQDs and peptides to form an AuNP-PEP@GQD (chemosensor 96) nanosensor. In the absence of CN-, the fluorescent emission of GQD was significantly diminished due to FRE facilitated by AuNPs, while the addition of CN led to the disassembly of 96 and the fluorescence recovery of GQDs. The LOD under optimal conditions was 0.52 µM (Fig. 27b). 168 In addition, a fluorescent chemosensor (97) based on BN co-doped GQDs (BN-GQDs) could sensitively detect paraguat in environmental water. Under UV light irradiation, the samples emitted different colors including green (B0), light green (B1), light blue (B2), and blue (B3). With an increase in the concentration of paraquat, the fluorescence intensity of 97 gradually diminished with the LOD of 0.0062 mg L^{-1} (Fig. 27c). 97 could specifically recognize paraquat by forming 97-(paraquat)_x intermediates, causing aggregationcaused quenching owing to π - π stacking. Fluorescence sensing based on graphene quantum dot chemosensors was also capable of detecting fenoxycarb, furan, glyphosate, and methylphosphate in water or vegetable samples with high efficiency (chemosensors **98–100**). 170–172 Among them, **99** showed the highest sensitivity for the detection of glyphosate. After the addition of glyphosate, the fluorescence of cysteine-capped AgNPs of 99 was quenched, implying that this chemosensor has high potential for testing enzymatic activity. Therefore, the low toxicity and high biocompatibility of GQDs provide an important tool for detecting factors that affect plant health.

GQDs show strong fluorescence characteristics, high solubility, excellent biocompatibility, low toxicity and photostability, but they also have some disadvantages, as follows: (i) the structure of GQDs is too small, and then not enough QY can be produced by chemosensors; (ii) the redox reaction and coordination of recognition parts cause GQDs to have weak antiinterference and poor specificity; and (iii) the synthesis process of GQDs is complex and requires many solvents that can increase their synthesis cost and toxicity.

4.1.4 Silicon quantum dots. Si QDs are a new type of fluorescent chemical sensing material with high fluorescence QY, which have been widely used in monitoring plant metabolites, heavy metals and pesticides in water. 194 For example, in recent years, it has been reported that a cyanine-colored luminescent Si QD chemosensor (chemosensor 101) could accurately monitor the endogenous plant metabolite chlorogenic acid (CGA) with good stability and fast response. The optimal engagement and emissive radiation wavelengths for 101 were 350 nm and 470 nm, respectively. Chlorogenic acid quenched the fluorescence of 101 through the synergistic action of static

Review Article

a b Bright field Overlay 3.0e+ C N-doped GQD ntensity I.atio, F₀/F(a.

Fig. 27 Schematic representation of graphene-based quantum dot chemosensors for detecting water pollution. (a) Hydrophilic graphene quantum dot chemosensor for the detection of heavy metals Hg^{2+} , Cd^{2+} , and Pb^{2+} in water. Copyright © 2021, Elsevier. (b) Novel dual-photo-excitation nanofluorescent sensor with GQD/AuNP conjugates for the detection of CN⁻ in plants. 168 Copyright © 2015, the American Chemical Society. (c) Microwave synthesis of boron and nitrogen co-doped graphene quantum dot fluorescent chemosensors for the detection of paraguat in aqueous media. 169 Copyright © 2023, Elsevier.

97

and dynamic quenching, and it was used for the in situ detection of chlorogenic acid in coffee beans. The LOD was $0.43\ \mu mol\ L^{-1}$ and the recoveries were in the range of 99.96– 109.20% (Fig. 28a). 173 Novel S-doped Si QDs (chemosensor **102**) capable of detecting Fe³⁺ in water were reported, which exhibited an optimal emission of 425 nm at an excitation wavelength of 345 nm, and blue fluorescence under UV illumination. When subjected to numerous metal ions, Fe3+ exhibited a linear quenching effect on the fluorescence intensity of 102, which

Boric acid

was utilized to detect Fe3+ in water. The linear range was 1-20 μM and the LOD was 0.21 μM (Fig. 28b). ¹⁷⁴ Fluorescent chemosensor (103) based on Si QDs also enabled the accurate detection of Hg²⁺ and Cu²⁺ in water. 175

Upon the addition of Hg2+, the fluorescence intensity of 103 decreased rapidly, which could be recovered by coordination with glutathione. The linear range for the detection of glutathione and Hg²⁺ was 0.1-5 μM and 0.1-4 μM, with LODs of 55 nM and 24 nM, respectively. The results indicated that the

chemosensor can monitor plant health under ion stresses. In addition, sensing centers based on Si QDs, gold nanoparticles (AuNPs) and CdTe QDs (chemosensor 104) detected carbaryl in lake water and in apples. The blue Si QDs showed an emission spectrum at 460 nm, whereas the red-light emitting CdTe QDs showed an emission peak at 650 nm. Carbaryl exhibited a tendency to adsorb on AuNPs, eliciting a gradual increase in

the fluorescence emission intensity of the Si QDs, while simultaneously inducing a notable reduction in the fluorescence emission intensity of 104. The LOD of carbaryl in lake water and vegetable samples containing carbaryl was 3.3 nM in the concentration range of $80-200 \mu M$. Importantly, it could be detected in real-time by a smartphone sensing platform (Fig. 28c). Therefore, the proposed sensing scheme enables

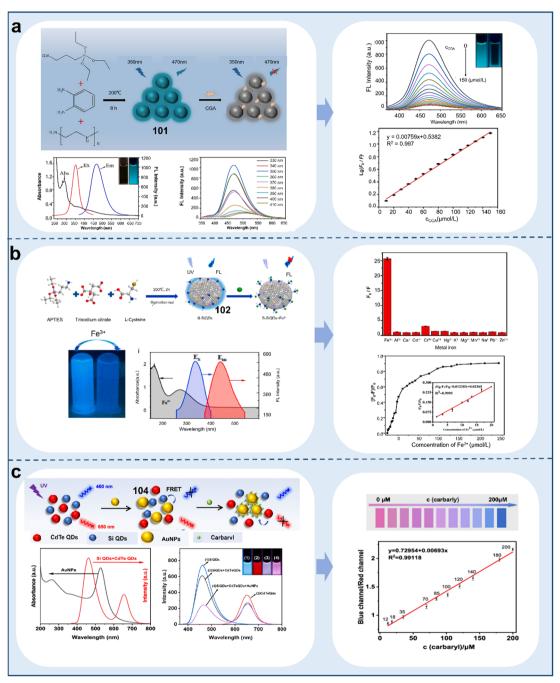


Fig. 28 Schematic representation of silicon quantum dot-based chemosensors for monitoring the living environment and quality of plants. (a) Cyanoluminescent Si quantum dot fluorescent chemosensor for the detection of chlorogenic acid. 173 Copyright © 2023, Elsevier. (b) Detection of Fe²⁺ in water by S-doped Si quantum dot chemosensor.¹⁷⁴ Copyright © 2020, Elsevier. (c) Detection of carbaryl in vegetables by a fluorescent sensor with amino-modified gold nanoparticles, blue-emitting silicon quantum dots and red-emitting cadmium telluride quantum dots. 176 Copyright © 2023, the American Chemical Society.

new proportional fluorescence detection with satisfactory specificity and sensitivity, paving the way for implementing smart phone-centric pesticide detection platforms.

Si QDs have some advantages such as high QY, abundant silicon source, low toxicity and environmentally friendly nature, but they also have disadvantages, as follows: (i) the low water solubility of Si QDs limit their application in biological imaging and decrease their sensitivity and (ii) the poor stability and easy coacervation of Si QDs can affect their fluorescence efficiency, which can be improved by modifying their surface.

4.1.5 Molybdenum disulfide quantum dots. MoS₂ QDs are two-dimensional (2D) inorganic graphene analogs that have been used to identify phytohormones, heavy metals and pesticides in the living environment of plants. 195 For example, novel Eu³⁺ ion-functionalized fluorescent molybdenum sulfide QDs (Eu-MoS₂ QDs) (chemosensor 105) were used for the effective detection of guanosine 3'-diphosphate-5'-diphosphate (ppGpp). 105 showed bright-blue fluorescence with optimal excitation and emission wavelengths of 310 and 410 nm, respectively. The electrostatic interaction of the negatively charged ppGpp with positively charged Eu-MoS2 was stronger for these QDs than for other QDs, and thus the substantial enhancement in red fluorescence was rapid when ppGpp was added to the solution with an LOD of 23.8 μM (Fig. 29a). 177 MoS₂ QDs can also be combined with manganese dioxide using nanosheets to design "off-on" chemosensor 106 to determine trace levels of ascorbic acid (AA).178 Upon the addition of ascorbic acid, the fluorescence of 106 was gradually restored, which mainly depended on the reducibility of ascorbic acid. Considering that there are many reducing substances in plants, a specific reaction unit should be added to increase the selectivity of **106**. Another MoS₂ OD chemosensor (107) was also able to achieve the sensitive detection of Pb²⁺ in water. When excited at 440 nm, the MoS₂ QDs exhibited the maximum intensity at 360 nm, which redshifted with a change in the excitation wavelength. The linear detection range in aqueous solution was 3.3×10^{-7} to 8×10^{-3} M with an LOD of 3.5×10^{-3} M (Fig. 29b). This type of chemosensor also enabled the fluorescence detection of Hg²⁺ in water (chemosensor 108). 180 Compared with the substitution reaction mechanism, 108 combined with Hg²⁺ showed a synergistic effect for the reaction between TMPvP and Co²⁺, which caused an evolution in its optical characteristics and promoted the Hg²⁺ sensing to the nM level. A β-cyclodextrin-functionalized MoS₂ QD nanochemosensor (109) was reported for the sensitive fluorescence detection of methylthiophene (MP). 109 showed shifted excitation and emission peaks compared to MoS₂. The fluorescence intensity of 109 gradually decreased with an increase in MP concentration, and there was good linearity in the MP concentration from 0.01 ppm to 18.0 ppm with an LOD of 3.3 ppb (Fig. 29c).¹⁸¹ Therefore, MoS₂ QDs need to be continuously explored to find more robust and effective methods for improving their biological applications.

MoS₂ QDs have been widely used to detect ions and pesticides in the living environment of plants owing to their high QY, biocompatibility, and low toxicity, but their applications are limited due to the following facts: (i) most MoS2 QD-based

biosensors are turn-off fluorescence sensors, and their fluorescence signal is susceptible to the detection system, which may lead to incorrect detection results and (ii) the processes for the synthesis of MoS₂ QDs are complex, which lead to a low yield, size various, and difficult removal of organic solvents.

4.1.6 Sulfur quantum dots. S QDs consist of a polymer core of sulfur and substantial surface functional groups, presenting superior optical stability and tunability, which have been employed for detecting heavy metals in plants. 196 S QDs (chemosensor 110) with good water solubility and stability were prepared via a simple one-step method. UV irradiation at 320 nm resulted in 110 showing the maximum emission peak at 431 nm and blue fluorescence with a QY of about 71%. The distinct reduction in the blue fluorescence emission intensity of 110 was noticeable due to the presence of Co²⁺. The feasibility of the assay was evaluated using the rhizome of Salvia miltiorrhiza as a sample, and the protocol was found to have good recoveries and relative standard deviations for the determination of Co²⁺. The LOD was 4.51 µM when the concentration of Co²⁺ was 5-50 μM (Fig. 30a). 182 Fluorescence sensing technology based on S QDs could also selectively detect Hg²⁺, Fe³⁺ and Cu²⁺ in water samples (chemosensor 111 and 112). 183,184 111 showed excellent reducibility and it could reduce Cu2+ and Fe3+ to Cu+ and Fe2+, respectively, which indicated that 111 may be an effective tool for detecting the redox state transition of ions. 183,184 In addition, the first hydrothermal preparation of S QDs combined with rhodamine B (RhB) resulted in a novel sensing platform (chemosensor 113) with dual-emission, which could be used to quantitatively monitor 2,4-dichlorophenoxyacetic acid (2,4-D) in vegetables. When excited at 380 nm, 113 produced two emission peaks at 455 nm and 580 nm. The SQD and RhB-SQD solutions appeared transparent light-yellow and light-pink under the sunlight, respectively, and blue or pink-purple color under 365 nm UV irradiation. 113 was successfully used to determine the content of 2,4-D in vegetable and water samples with an LOD of 17.3 ng mL⁻¹ (Fig. 30b). 185 This enzymatic inhibitorbased analytical technology provides an uncomplicated efficient way for evaluating the concentration of pesticides in vegetables.

S QDs have been widely used to image ions in plants owing to their high fluorescence intensity, low toxicity and photostability, while they also have some disadvantages, as follows: (i) the temperature instability of S QDs implies that they can be developed as a temperature sensor and (ii) the excitation wavelength of S QDs is mainly in the blue region, which limits their application in biological imaging.

4.1.7 MXene quantum dots. Recently, the emerging development of MXene QDs, mainly in combination with smart devices, has enabled the real-time monitoring of heavy metals and harmful organics in the living environment of plants. 197 For example, a two-dimensional MXene QD-based fluorescent chemosensor (114) could simultaneously monitor and remove the heavy metal Mn(vii) from plant leaves. Upon exposure to 365 nm excitation, 114 showed predominant bright blue-green fluorescence with emission and excitation peaks located at 473 nm and 320 nm, respectively, which was primarily ascribed to both its inner core and inherent defects. 114 exhibited ultra-

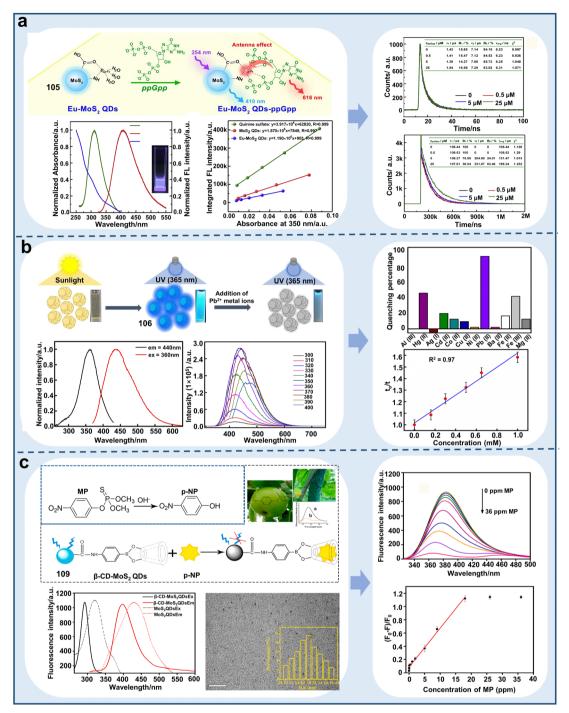


Fig. 29 Schematic representation of molybdenum disulfide-based quantum dot chemosensors for detecting ions and pesticides in plants or the environment. (a) Eu-doped MoS₂ quantum dot fluorescent chemosensor developed for paper sensor detection of ppGpp. 177 Copyright © 2020, Elsevier. (b) Functionalized molybdenum disulfide quantum dot fluorescent chemosensor for the detection of Pb²⁺ in water to determine its quality. 179 Copyright © 2020, Elsevier. (c) Detection of p-methyl parathion in fruits by β -cyclodextrin-functionalized molybdenum disulfide quantum dot fluorescent chemosensor. ¹⁸¹ Copyright © 2021, Elsevier.

sensitivity and selectivity towards Mn(vII), which resulted in a marked diminution in its fluorescence intensity. 114 exhibited bright fluorescence in the leaves, which disappeared upon the injection of Mn⁷⁺. The results revealed that **114** is an effective fluorescent chemosensor for detecting the concentration and distribution of Mn⁷⁺ in plants with an LOD of 230 nM. The efficacy of Mn⁷⁺ elimination employing 114 was ascribed to its self-reductive potential, thereby facilitating the removal of Mn⁷⁺ (Fig. 31a). 186 The results indicated that 114 has dual function for monitoring the presence of heavy metals and removing heavy metals from the environment or plants. Fluorescence sensing based on MXene QD chemosensors also enabled the accurate detection of Cr3+ and Cu2+ in water (chemosensors 115 and 116, respectively). 187,188 115 was composed of N-doped

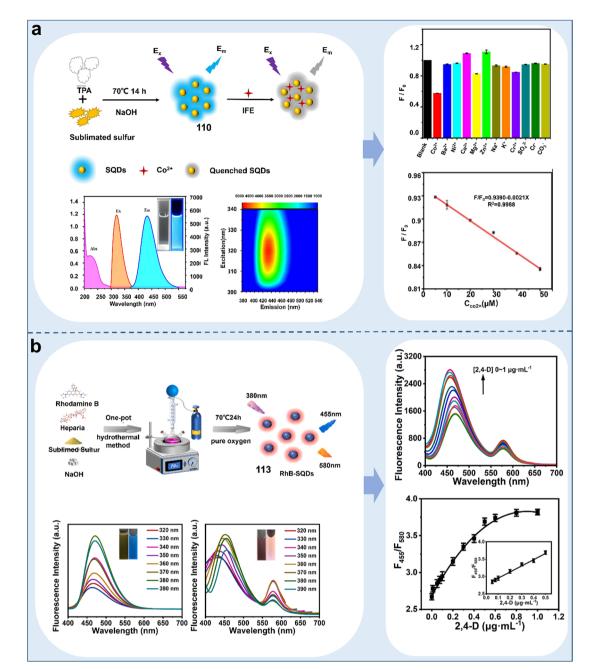


Fig. 30 Schematic representation of sulfur-based quantum dot chemosensors for detecting ions and pesticides in plants and water. (a) Detection of Co²⁺ in water by a sulfur quantum dot fluorescent chemosensor. ¹⁸² Copyright © 2023, Elsevier. (b) Novel dual-emission sulfur quantum dot fluorescent chemosensor enables the accurate detection of 2,4-dichlorophenoxyacetic acid. 185 Copyright © 2023, Elsevier.

Ti₃C₂ MXene QDs and N doping showed a positive correlation with the size of QDs. 115 showed different fluorescence quenching by interaction with various metal ions, which could specifically recognize Cu2+ based on the static fluorescencequenching mechanism. Recently, nitrogen-doped MXene QDs (chemosensor 117) were reported for the detection of alizarin red (ARS) in water at 420 nm when excited at 580 nm. The MQD solution was light yellow in daylight and showed strong yellow fluorescence at 365 nm UV. As the concentration of alizarin red increased, the fluorescence of 117 gradually decreased due to the inner-filter effect (IFE). The linear range and LOD were 0-80 μM and 1.21 μM in real water samples, respectively (Fig. 31b). 198 In addition, Ti₃C₂ MXene QDs (chemosensor 118) based on uronic acid encapsulation also enabled the fluorescence detection of 2,4,6-trinitrophenol in water. 189 TNP could significantly quench the fluorescence of 118 by the IFE, showing a good linear concentration range of 0.01-40 µM and LOD of 9.58 nM. Considering the more environmentally friendly and water-soluble nature of 118, further studies should focus on combining a smartphone with this fluorescent system, which can realize the easy and convenient detection of 2,4,6trinitrophenol in the environment. The novel material, MXene

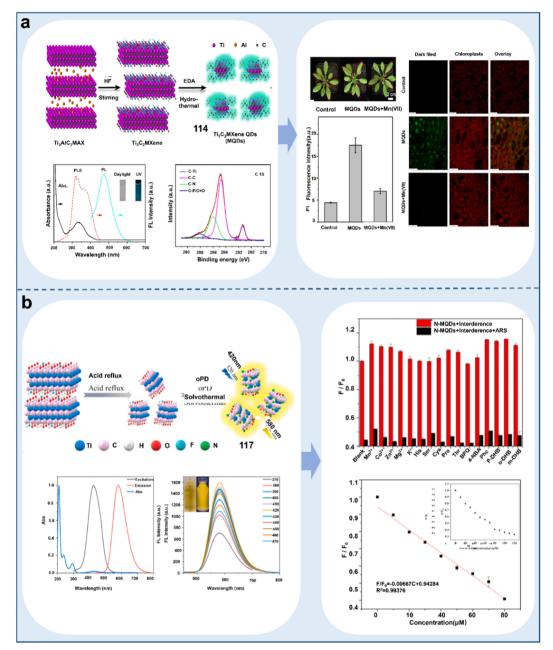


Fig. 31 Schematic diagram of the application of MXene quantum dot-based chemosensors for the detection of ions in water and plants. (a) Accurate detection of Mn(vii) in water and plants based on MQD fluorescent chemosensors. ¹⁸⁶ Copyright © 2023, Elsevier. (b) Solvothermal synthesis of N-MQD fluorescent chemosensors for the detection of ARS in real water samples. ¹⁹⁸ Copyright © 2021, Elsevier.

QDs, offers an important solution for both monitoring and removing metal ions in the environment, which has great potential for improving the quality of the living environment of plants.

We summarized the application of MXene QD chemosensors in detecting the factors affecting or reflecting plant health, which showed good detection efficiency in these areas. However, there are some disadvantages that need to be improved, as follows: (i) almost all MXene QD chemosensors showed UV or blue excitation light, which can reduce the application of these chemosensors for detecting plant hormones, proteins, or enzymes; (ii) the synthesis

strategies for MXene QDs chemosensors should be improved such as fluorine-free or high efficiency and stability of catalyst, which can reduce the toxicity of MXene QD chemosensors and increase their application scope; and (iii) combining MXene QD chemosensors with smart devices to improve the detection and removal efficiency, which will be the future development direction.

4.2 Metal-organic frameworks (MOFs)

MOFs are a class of coordination polymers self-assembled with metal centers (clusters) and organic ligands through coordination bonds. Due to their superiorities of adjustable metal ion

species, diverse functional sites and clear structure, MOFs have emerged as exciting sensing and detection materials. 200,201 A distinctive approach for the fabrication and design of luminescent MOFs (LMOFs) involves utilizing the porous nature of the MOF host to encapsulate diverse luminescent guests (LG), leading to the formation of a composite system known as "LG@MOF". 202 LG are mainly derived from metallic constituents, organic linkers and encapsulated guest entities (e.g., lanthanide ions, organic dyes and QDs) within MOFs.²⁰³ Besides, organic ligands with versatile reactive functional groups such as free pyridyl, imidazole, hydroxyl, and carboxyl groups, have been skillfully immobilized on the pore surfaces of fluorescent MOFs. This strategy aims to amplify the fluorescence sensing ability of MOFs by facilitating a wide array of host-guest interactions.204 Based on the differences in guest molecules, the main types of LG-MOFs include organic dyes@-MOF, metal ions@MOF, metal nanoclusters@MOF, quantum dots@MOF and perovskites@MOF. 204-207 Thus far, LMOF-based detection platforms have been developed to evaluate the living environment of plants (Fig. 32). Table 8 lists some classic examples of various developed MOF-based fluorescent chemosensors applied in this field.

4.2.1 Metal ion@MOF-based fluorescent chemosensors. Luminescence in metal ions is primarily observed in lanthanide ions, which is attributed to their substantial Stokes shift values, prolonged fluorescence lifetimes, visually discernible colors, superior quantum efficiency and narrow emission spectra. The distinctive fluorescence characteristics of Ln-MOFs originate from not merely from their 4f-4f electron transitions, but are additionally comprised of ligand-to-metal energy transfer (LMET), commonly referred to as the "antenna effect". 240 The organic linker of MOFs offers great tunability, enabling the effective interaction between MOFs and Ln ions. This interaction promotes energy transfer or establishes an optical antenna effect. thereby increasing the luminescent efficiency of Ln ions. Importantly, the inherent porous structure of MOFs offers a conduit for encapsulating guest materials, and the synergistic interplay between the host framework and the guest, including π - π interaction, hydrogen bonding, and coordination bonds, exhibit exceptional analytical sensitivity towards target analytes.241 Together, these factors have potential to significantly enhance the OY to approximately 14-30%. 218 Eu³⁺ and Tb³⁺ are the commonly used Ln ions to construct LMOFs. Non-Ln ions such as Zr^{2+} , Al^{3+} , Zn^{2+} and Cu2+ have also been documented for use as metal centers or transition components of MOFs. According to the investigations in the literature, LMOFs based on metal ions predominantly specialize in environmental monitoring, particularly in detecting pesticides, anions and cations (e.g., heavy metal ions). 209,212,242

 Eu^{3+} @MOF-based fluorescent chemosensors. Among the metal ions, Eu³⁺ ions are most commonly used to dope MOFs or as

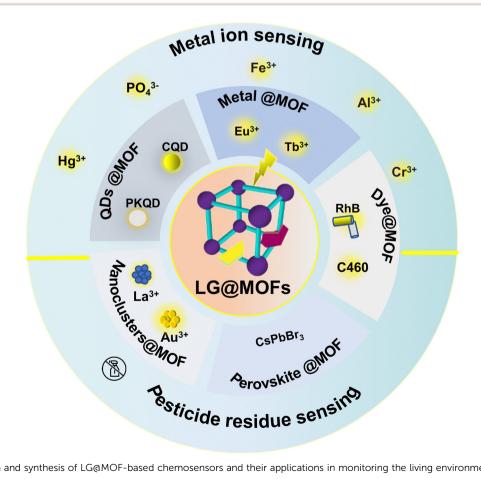


Fig. 32 Classification and synthesis of LG@MOF-based chemosensors and their applications in monitoring the living environment of plants.

Table 8 Examples of metal@MOF-based sensors for monitoring the living environment of plants

5							
nanonuorescence sensors	Chemosensors Name	sors Name	Linear range	(LOD)	Target analytes	Applications	Ref.
Metal ions@MOF Lanthanide 119	anide 119	Eu-MOF	I	0.280 μM for Fe ³⁺ ,	Fe ³⁺ , Fe ²⁺ , Cr ₂ O ₇ ²⁻	Detection of Fe ³⁺ , Fe ²⁺ , and $Cr_2O_7^{2-}$ in water	208
	120	Eu-MOF	0–110 and 0–90 μM	0.120 μ M for Fe ³⁺ , 0.360 μ M for Al ³⁺	${\rm Fe}^{3+}$, ${\rm Al}^{3+}$	ing the concentration of Fe ³⁺	, 209
	121	Eu-MOF	0.02-200 µM	2.60 nM	$^{+}$	Detection of Hg ²⁺ in water	210
	122 123	Eu-MOF Eu-MOF	1 1	$10^{-5} \; ext{mol L}^{-1} = 0.170 \; \mu ext{M}$	PO_4^{5-} Pesticide DCNA	Detection of PO ₄ in water Monitoring the concentration of	$211 \\ 212$
	ç	H 000	- 1 cm 200 00 00 00 00 00 00 00 00 00 00 00 00	1 400 50 11-1	Coup and arrive (CDZ)	pesticide DCNA in water	5
	125	Tb-MOF	0.06^{-4} and 4^{-40} µg int $0-80$ µg L^{-1}		Carbendazini (CBZ) Thiabendazole (TBZ)	Detection of TBZ in apples and tea Detection of TBZ in orange samples	214
	126	Tb-MOF	$10 1000 \; \mathrm{ng} \; \mathrm{mL}^{-1}$ —	3.41 ng mL^{-1}	Chlorpyrifos Flavonoids stilhenes	Detecting CPF in fruit juice Monitoring the concentration	214
		, in the case of t			anthraquinones	changes of	2
					,	saponnis, navonojus, supenes, anthraquinones in plant	
	128	Tb-MOF		4.50 ppm	PO_4^{3-}	Detection of PO_4^{3-} in water	216
	130	Ce-MOF	$0.02-30~ m \mu g~mL^{-1}$	$0.100~ m ppm \ 0.00620~ m \mu g~mL^{-1}$	FO ₄ Glyphosate	Detection of glyphosate in water $\frac{1}{2}$	217
	131 132	Al-MOF Zn/Fe-MOF	$^{-0}_{0.001-100}~{ m mg}~{ m L}^{-1}_{0.001}$	$102~ m nM$ 0.340 $ m \mu g~L^{-1}$	Pd** Paraquat (PQ)	Detection of Pd*' in water Monitoring the content of PQ in	219 220
						cabbage and agriculture irrigation	
	133	UiO-66(Zr MOF)	$0-200 \mu M \text{ for } \mathrm{Cr_2O_7}^{2-},$	0.160 µM for	${ m Cr}^{3+} \left({ m Cr}_2 { m O_7}^{2-} / { m Cr} { m O_4}^{2-} ight)$	water Detecting the concentration of Cr ³⁺ in 221	1 221
			ć	$Cr_2O_7^-$, 0.170 μM for $CrO_4^{\ 2-}$		ГООД	
	134	Mn/Fe-MOF	$0-220 \mu M \text{ for } \text{CrO}_4^{2-} \ 10^{-9} - 10^{-7} \text{ M}$	0.850 nM or 0.290	Glyphosate	Detection of glyphosate in water	222
Quantum dots@MOF	135	Cu-MOFs@CDs	$0.0307 - 0.769 \; \mu mol \; L^{-1}$	$\begin{array}{c} \mathrm{ppb} \\ \mathrm{3.67~nmol~L^{-1}} \end{array}$		Microcystin-LR	223
,	136	MOF-5@CH ₃ NH ₃ PbBr ₃ CDs		I	AI^{3+} , Bi^{3+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Cd^{2+}	Monitoring various ions in water	224
	137	MOF-derived In_2O_3 hollow tubulars (aTi ₃ C, ODs	$0.5 ext{-4} imes10^5~ ext{pmol L}^{-1}$ s	$0.169~\mathrm{pmol~L}^{-1}$	Photoelectrochemical (PEC)	Detection of PEC in water	225
	138	ZIF-8@ZnS QDs	Mu 08−0	Mμ 088.0	Chlorpyrifos	Detection of CPF in water	226
Organic dyes@MOFs	139 140	ZIF-67@ZnSQDs RhB@Zr-MOF	3-500 nM —	0.960 nM 1.60 µM for Fe ³⁺ ,	Cu^{2+} Cu^{3+} Fe^{3+} nitenpyram	Detection of Cu ²⁺ in water and soil Detecting the content of Fe ³⁺ and	227 228
				o.200 µm ror nitenpyram		nitenpyrani in water	
	141	RhB@HNU-48	I	0.590 ppb	Alachlor	Monitoring the concentration of alachlor in paddy water and soil, polished rice and cucumher	229
	142	RhB@Zr-MOF	I	6.27 for $Cr_2O_7^{2-}$,	${\rm Cr_2O_7}^{2-}, {\rm CrO_4}^{2-}$	Detection of $Cr_2O_7^{2-}$ and CrO_4^{2-} in	230
	143	Doxoruhicin@AzoMOF	0–5 119° mL, ⁻¹	5.26 ppb for CrO_4^{2-}	Dufulin	water Detection of dufulin in water	231
	144	Curcumin@MOF-5		3.10 µM for A- curcumin@MOF-5,	Al^{3+}	Monitoring the concentration of Al ³⁺ in lettuce extract and water sample	
				2.84 µM for B- curcumin@MOF-5		•	
Metal clusters@MOFs	145 146	AuNCs@ZIF-8 AuNCs@Zr-MOF	3-30 nM —	1.00 nM 193 pM	Нg ²⁺ Нg ²⁺	Detection of Hg^{2+} in food Detection of Hg^{2+} in water	233 234

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Fable 8 *(continued)*

Nonofliorecoance				Timit of dotooticy			
sensors	Chemosen	Chemosensors Name	Linear range	(LOD)	r Target analytes	Applications	Ref.
	147	AuNCs@ZIF-8	$0.75~\mu g~L^{-1}$ -100 mg L^{-1}	$0.300~{ m \mu g}~{ m L}^{-1}$	OPs	Detection of OPs in water	235
	148	AgNCs@Zr-MOF	$0.010-0.5 \mathrm{\mu g \ mL^{-1}}$ 1.80 $\mathrm{\mu g \ L^{-1}}$	$1.80~\mathrm{\mu g~L^{-1}}$	Hg^{2+}	Detection of OPs in water	236
	149	CuNCs@MOFs UiO-66-	-66- 1-30 μМ	178 nM	Cu^{2+}	Detection of Cu ²⁺ in water	237
		$(COOH)_2$					
	150	LaNCs@MOFs	16.6–167 μM	16.6 µM	Fe^{3+}	Detection of Fe ³⁺ in water	238
Perovskite@MOFs	151	Eu^{3+} $\mathrm{@CsPbBr}_{3}$	0-1 µM	0.116 nM	Hg^{2+}	Detection of Hg ²⁺ in water	239
		nanocrystal					

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atomic centers for the construction of single emission or double emission fluorescent chemosensors to detect harmful anions and cations in the living environment of plants.²⁴⁰ For instance, Xu et al. introduced Eu³⁺ in the MIL124 MOF to develop a highly selective and sensitive single-emission chemosensor (Eu³⁺@ MIL124, 119) for the detection of Fe^{2+} , Fe^{3+} , and $Cr_2O_7^{2-}$ via the exceptional fluorescent quenching exhibited by Eu3+ and MOF compared to other metal ions.²⁰⁸ However, although the single luminescence based on MOFs is easily measured, 204 their intensity is often interrupted by the concentration and environment of chemosensors. In this case, the incorporation of two or more emitting sites resulting from the dual emission or bimetallic properties of Ln metal ions and organic ligands can effectively avoid false responses, thereby improving the S/N ratio.²⁴⁰ For example, Xia et al. successfully developed a novel dual-emission MOF incorporating Eu3+ ions and 2-hydroxyterephthalic acid (H₂BDC-OH) in a UiO-66-type MOF material (chemosensor 120).²⁰⁹ 120 displayed dual emission peaks at 450 and 614 nm and exhibited good anti-interference characteristics for Fe³⁺ and Al³⁺ in the complex aquatic environment. Besides, 120 exhibited remarkable selectivity and sensitivity towards Fe³⁺ and Al³⁺, and their detection linear range was 0-110 and 0-90 μM, respectively (Fig. 33a). Additionally, Hao et al. successfully synthesized a dual-emission Ln-MOF material (Eu-Ca-MOF) by incorporating Eu³⁺ ions in the channels of a Ca-MOF parent framework (chemosensor 121).210 121 exhibited excellent PL properties, in tandem with precise capacity to detect trace levels of Hg²⁺ in water, achieving an LOD of 2.6 nM (Fig. 33b). Besides, a novel Eu-based three-dimensional framework was obtained based on the 1,3,5-benzenetribenzoate (H₃BTB) ligand with high C_3 symmetry (chemosensor 122).²¹¹ 122 demonstrated remarkable thermostability and water stability for the detection of PO₄³⁻ ions among various colorless anions. This work represents a pioneering example of regenerable MOF-based luminescent chemosensors for detecting PO₄³⁻. Besides monitoring harmful ions, Eu-MOF-based chemosensors have also been used for detecting pesticide residues. For example, Qin et al. designed ultrathin fluorescent Eu³⁺@Zn-MOF nanosheets (Eu³⁺@Zn-MOF-NS, chemosensor 123) to rapidly detect the residues of organic pesticides. ²¹¹ In the synthesis of 123, 2,6-dichloro-4-nitroaniline (DCNA) was employed, utilizing Zn2+ as the metal node and pyridine and 1,4-benzenedicarboxylate (H₂BDC) (Py) as the organic ligands. 123 offered a unique combination of benefits of both MOFs and 2D nanomaterials simultaneously. Notably, its LOD and K_{sv} were 0.17 μ M (35 ppb) and 3.2 \times 10⁵ M⁻¹ in water, respectively. 123 could potentially be applied for the rapid, in situ, and visualized detection of DCNA residues on fresh vegetables (Fig. 33c). The intense PL exhibited by 123 could be significantly quenched by DCNA in water, without any interference from other amino acids, small organic molecules, pesticides, or commonly encountered anions and ions. Interestingly, the asobtained Eu³⁺@Zn-MOF-NS probe in this work is promising for the visual, rapid, and in situ detection of DCNA residues on fresh vegetables. This work provides meaningful information on using Eu3+-based MOF probes for the effective detection of

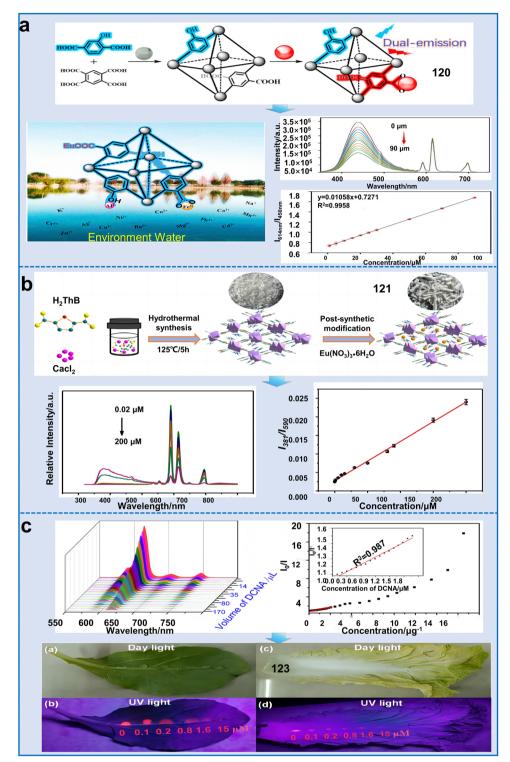


Fig. 33 Applications of Eu³⁺-based sensors for monitoring the living environment of plants. (a) Synthesis of a highly water-stable dual-emission Eu³⁺loaded MOF (EuUCH) and its detection of Fe³⁺ and Al³⁺ metal ions. ²¹⁰ Copyright © 2022, Elsevier. (b) Synthesis of Eu-Ca-MOF fluorescence sensor and its detection sensitivity for Hg²⁺ in water.²¹¹ Copyright © 2022, Elsevier. (c) Detection sensitivity of Eu³⁺@Zn-MOF for pesticide and its sensing effect in actual samples. 211 Copyright © 2022, the American Chemical Society.

pesticide residues in practical applications. However, although Eu³⁺-based sensors have been applied in environment monitoring, related studies on bioimaging in plants are still lacking.

*Tb*³⁺@*MOF-based fluorescent chemosensors.* In addition to the incorporation of Eu³⁺ ions mentioned earlier, other commonly used Ln ions such as Tb³⁺ have been extensively employed in the

construction of LMOFs to detect natural metabolites, metal ions and pesticide residues. For example, Wang et al. successfully fabricated a fluorescent nanosheet of a two-dimensional terbiumbased MOF (2D Tb-MOF) for the detection of carbendazim (CBZ) (chemosensor 124). 213 The 2D Tb-MOF nanosheets, synthesized with 5-borono-1,3-benzenedicarboxylic acid (BBDC) and Tb³⁺ ions as the precursors, demonstrated outstanding optical features. After the addition of CBZ, the fluorescence of the Tb-MOF nanosheets was quenched due to dynamic quenching and the inner filter effect (IFE). 124 offered two linear ranges of 0.06–4 $\mu g~mL^{-1}$ and 4–40 $\mu g~mL^{-1}$ with an LOD of 17.95 $ng~mL^{-1}$

(Fig. 34a). Furthermore, the developed sensing platform was

effectively utilized to detect CBZ in apples and tea samples, yielding satisfactory results. However, in the presence of other

coexisting substances such as NH4+, glucose and fipronil, the

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reaction between Tb-MOF and CBZ was slightly hindered. Another study constructed a highly selective luminescent sensor (chemosensor 125) for monitoring thiabendazole (TBZ) in oranges based on a Tb³⁺-functionalized Zr-MOF (Tb³⁺@1). 125 with high selectivity exhibited a good linear range of 0-80 μM, rapid response time (less than 1 min) and LOD of 0.271 μM. Additionally, this sensor presented good recoveries from 98.41% to 104.48% when used for detecting TBZ in real orange samples and this process only took 35 min (Fig. 33b). Coupling antibodies or aptamers with Tb-MOFs was helpful for the detection selectivity and sensitivity by providing specific recognition sites to match the target analyte molecules. 214 Another mesoporous molecular imprinted polymer (mMIP) layer imprinted Tb-MOF (MOF-76) fluorescent chemosensor (126) was constructed for the analysis of chlorpyrifos in fruit juice and the environment. 214 126

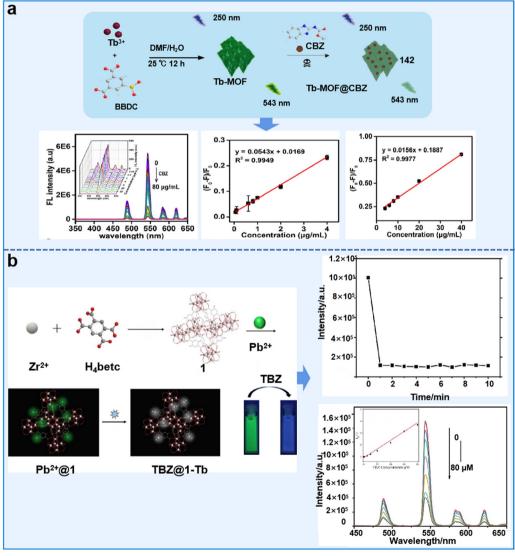


Fig. 34 Examples of Tb-MOF chemosensors for sensing pesticide residues. (a) Synthesis process of Tb-MOF@CBZ and its sensing effect and sensitivity for CBZ. 213 Copyright © 2023, Elsevier. (b) Synthesis process of Tb3+-functionalized Zr-MOF and its sensing mechanism and sensitivity for TBZ. 214 Copyright © 2021, Elsevier.

contained specific sites for the adsorption of chlorpyrifos, ensuring the selectivity of the designed chemosensor. It exhibited a linear response in the concentration range of 10–1000 ng mL $^{-1}$ for chlorpyrifos, with an LOD of 3.41 ng mL $^{-1}$. These studies provide useful analytical tools for the rapid and sensitive detection of CPF in the living environment of plants.

Besides the detection of pesticides, Tb-MOF chemosensors have also been used to monitor the distribution and concentration of inorganic anions and plant metabolites. For example, Yin *et al.* designed a fluorescent chemosensor (127) that incorporated Eu³⁺ and Tb³⁺ ions within an MOF. 127 enabled the rapid identification of various natural compounds, including 7 flavonoids, 12 saponins, 4 anthraquinones and 3 stilbenes.²¹⁵ 127 possessed powerful identification and analysis ability, and

the detection accuracy of each type of compound was up to 100% (Fig. 35a). Another study developed a Tb-MOF-based fluorescent chemosensor (128) for the detection of PO₄^{3-.216} 128 was demonstrated to be an exceptional luminescent chemosensor with a low detection limit, rapid response time, and an extensive detection range. Its versatile capabilities enabled the recognition of anions in water or other highly polar solvents, providing exciting prospects for various applications. Ji *et al.* encapsulated the Tb³⁺ cation into a 3D microporous MOF to construct a fluorescent-functionalized Tb@Zn-MOF (chemosensor 129).²¹⁷ 129 showed both excellent chemical stability and the characteristic emission of Tb³⁺. 129 emerged as an advantageous photoluminescent reagent demonstrating exceptional specificity and precision for the quantitative analysis of

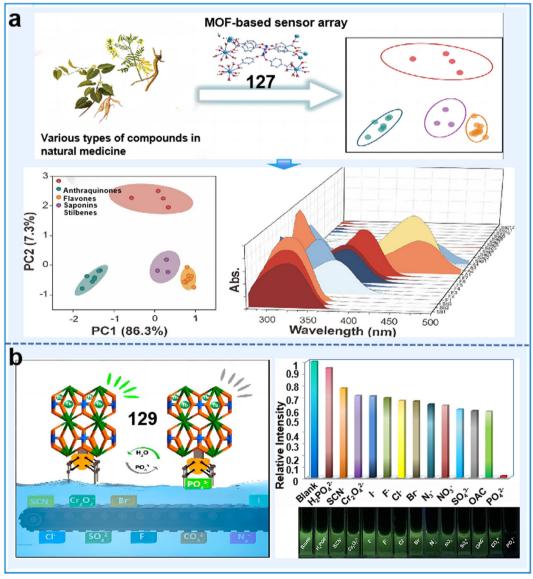


Fig. 35 Examples of Tb-MOF chemosensors for sensing ions and plant metabolites. (a) Schematic diagram of Ln-MOF-based sensor arrays for the identification and detection of natural compounds.²¹⁵ Copyright © 2021, the American Chemical Society. (b) Sensing sensitivity of Tb-MOF chemosensor for inorganic anions.²¹⁷ Copyright © 2018, the American Chemical Society.

PO₄³⁻. It presented a swift response time of only 10 s with a noteworthy LOD of 0.1 ppm. This investigation served as the pioneering prototype of a competent excitable fluorescent sensor to quantitatively assess the concentration of PO₄³⁻ in simulated biological systems and detecting its presence in aquatic environments with a broad concentration range of 10^{-6} to 10^{-3} M (Fig. 35b). This sensor offers a new approach for identifying inorganic anions, which is highly significant in both physiological and ecological settings. It is evident that metal ion@LMOF sensors with high efficiency and sensibility for the detection of phosphorus anions in the living environment of plants are still lacking.

Other metal ion@MOF-based fluorescent chemosensors. In addition to Eu3+ and Tb3+, some other metal ions have also been doped in MOFs to construct fluorescent chemosensors. For example, a study prepared a nanocomposite LMOF, incorporating UiO-67 nanoparticles within the pores of carbonaceous materials isolated from a novel Ce-MOF (Ce-PC) for the fluorescent sensing of glyphosate (chemosensor 130).²¹⁸ The prevalent oxygen-bearing hydroxyl moiety (M-O-H) present in UiO-67/Ce-PC was capable of recognizing the phosphoryl moieties (-PO₃H₂) in glyphosate via ligand substitution and exhibited specificity toward glyphosate (Fig. 36a). Findings revealed that glyphosate could be reliably detected in cereal specimens

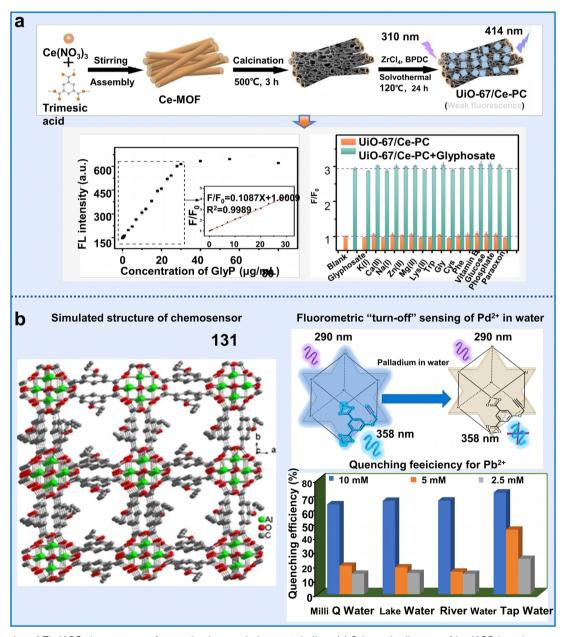


Fig. 36 Examples of Tb-MOF chemosensors for sensing ions and plant metabolites. (a) Schematic diagram of Ln-MOF-based sensor arrays for the identification and detection of natural compounds.²¹⁸ Copyright © 2021, the American Chemical Society. (b) Sensing sensitivity of Tb-MOF chemosensor for inorganic anions.²¹⁹ Copyright © 2018, the American Chemical Society.

in the concentration range of 0.02 to 30 µg mL⁻¹ with an LOD of 0.0062 μg mL⁻¹. These findings represent a promising approach for developing MOF-derived nanocomposite materials for the precise trace analysis of pollutants in the living environment of plants. Chakraborty et al. introduced an innovative ultrafast Al(III)-MOF chemosensor (131) for the detection of Pd²⁺.²¹⁹ 131 demonstrated the lowest response time (30 s) and a remarkable low LOD of 102 nM, which is the shortest response time for MOF-based Pd2+ sensing thus far. Compared to the previously reported palladium sensors based on MOFs, 131 exhibited excellent recyclability, maintaining consistent effectiveness and selectivity for Pd2+ detection over five cycles in real water with the same efficiency (Fig. 36b). The quick response, sensitivity, and selectivity of this sensor make it an excellent choice for the selective detection of Pd²⁺ ions in water. More importantly, we believe that this work based on the alkyne $-\pi$ interaction concept will inspire studies in diverse areas, particularly the development of various functionalized MOF-based sensors for detecting other hazardous heavy metal ions. Besides single metal doping, bimetallic-doped MOF-based sensors are promising to improve the sensing signal and sensitivity. For instance, Wu et al. developed an innovative electrochemical method for the detection of paraguat through the use of a modified glassy carbon electrode. The modification involved the incorporation of a Zn/Fe dual-metal ZIF-generated nanoporous carbon composite (Zn/Fe-ZIF-NPC) with Ni hexacyanoferrate nanoparticles (NiHCF-NPs) on the electrode substrate (chemosensor 132).220 NiHCF-NPs functioned as the dedicated signal chemosensor, whereas Zn/Fe-ZIF-NPC promoted swift electron transfer and powerfully amplified the discernible signal originating from NiHCF-NPs. Consequently, the modified electrode exhibited a linear concentration range of 0.001 to 100 mg L^{-1} and with an impressive LOD of $0.34 \mu \text{g L}^{-1}$. These outcomes provide strong evidence supporting the high reliability and application of the proposed methodology for discerning PQ contamination in actual vegetables and agricultural irrigation water. Besides the above-mentioned chemosensors, some other chemosensors based on metal-MOF could also detect anions, cations, and pesticides in the environment (chemosensors 133 and 134). 221,222

In summary, these results offer some available strategies for future studies to develop more effective and sensitive fluorescent chemosensors based on metal ion MOFs for monitoring the living environmental conditions of plants. However, although considerable results have been achieved, there are still some concerns in their actual application, as follows: (i) the use of Ln ions for constructing LMOFs is currently limited to a narrow range of options, and the Earth's supply of Ln ions is also restricted. These factors present obstacles to the widespread application of Ln-based MOFs. 204 (ii) The efficiency of exciting Ln ions through the excitation light is limited due to the forbidden nature of the 4f-4f electronic transition, and the generation of higher external quantum efficiency is hindered for Ln-ions. (iii) Most of the studies on metal ion@MOF sensors mainly focus on detecting pollutants and bio-small molecules in the living environment of plants, but there is still a lack of research on biological detection, such as plant hormones. (iv) To ensure successful sensing in water or other sensing media, it is crucial to enhance the stability of LnMOF-based sensors, particularly their water stability. This improvement is necessary to prevent structural breakdown or degradation before the sensing process is completed.240

4.2.2 Quantum dot@MOF fluorescent sensors. The chief design for OD-MOFs is a specific class of MOFs, wherein ODs are intercalated into the framework of MOFs or reside within their pores. The surface of the QDs offers multiple interaction sites, which substantially manifest alterations in their fluorescence intensity, serving as an integral component in the sensing mechanism. 243 Nevertheless, combining QDs with MOFs can mitigate agglomeration issues that may arise during precipitation and drying. This integration effectively suppresses electronic transition and cavitation, enhancing the stability of the QDs within the MOF framework.²⁰⁴ To date, a diverse range of QDs, such as carbon QDs, perovskite QDs, ZnS QDs, and Ti₃C₂ QDs, has been successfully integrated in MOFs.²²⁴ The following parts will elaborate on the application of these quantum dotbased MOF chemosensors in fluorescence detection.

In recent years, carbon dots (CDs) have attracted significant research interest in the field of sensing due to their remarkable attributes including low toxicity, tunability and robust fluorescence emission stability.244 The abundant functional groups on the surface of CDs facilitate their direct chemical coordination with MOFs.²²³ These phenomena indicate that integrating CDs with MOFs is a promising and efficient strategy for the detection of harmful substances in plant surroundings. For example, a simple and efficient ratiometric fluorescence chemosensor, CDs@Cu-MOF (135), was constructed for the detection of pesticide thiophanate-methyl (TM). This chemosensor was formed by coordinating the -COO- groups present on the surface of CDs with Cu²⁺ ions of Cu-MOF.²²³ 135 demonstrated excellent selectivity and accuracy for detecting TM in food samples, which was achieved through the interplay of π stacking and Cu²⁺ chelation between TM and Cu-MOFs and exhibited a remarkable LOD of 3.67 nmol L^{-1} . Therefore, CD-based MOF sensors present a novel and effective strategy for pesticide detection, offering potential applications in monitoring plant health.

Hybrid organic-inorganic halide perovskites, such as CH₃NH₃PbX₃ (X = Cl, Br, and I), have attracted significant interest in recent years. However, the practical use of CH₃NH₃PbX₃ is limited due to the intrinsic susceptibility of its organic cation CH₃NH₃⁺. Under diverse environmental conditions such as UV light, moisture, high temperatures, and oxygen this cation degrades rapidly.²²⁴ Accordingly, integrating CH₃NH₃PbX₃ QDs in MOFs can significantly improve their stability, and perovskites QD-based MOF fluorescent chemosensors have been successfully implemented to detect pesticides and heavy metal ions in the environment. Zhang et al. developed an innovative methodology for enhancing the stability of CH3NH3PbX3 perovskite QDs by encapsulating them within MOF-5 microcrystals. This was achieved by adding PbBr2 and CH3NH3PbX3 precursors in a stepwise manner to create a stable CH3NH3PbX3@MOF-5 composite (chemosensor 136).²²⁴ 136 demonstrated significantly

enhanced water resistance and thermal stability compared to CH₃NH₃PbX₃ QDs, which was useful for detecting various metal ions in water including Al3+, Bi3+, Co2+, Cu2+, Fe3+, and Cd2+ (Fig. 37a). However, although this work improves the relative stability of perovskite QDs, the exploration of the fundamental properties, operating principles, and prospective applications of CH₃NH₃PbX₃ QDs encapsulated in MOFs remains a limited and

Review Article

challenging area of research.

In addition to CQDs, Ti₃C₂ QDs are also excellent candidates for constructing fluorescent chemosensors due to their inherent hydrophilicity and conductivity originating from 2D MXene. Moreover, they offer advantages such as abundant active sites, enhanced redox activity, and excellent stability. Studies indicated that microcystin-LR (MC-LR) can inhibit the growth and reproduction of bacteria, aquatic animals, and some phytoplankton in water bodies, and thus the effective detection of MC-LR is very important. Yan et al. developed a self-powered aptasensing platform for the detection of MC-LR, which utilized a dual-mode approach combining photoelectrochemical (PEC) and photofuel cell (PC) techniques (chemosensor 137). 225 The platform utilized an In₂O₃-In₂S₃-Ti₃C₂ (IO-IS-TC) composite assembled on the base of MOF-derived In2O3 hollow tubulars, with Ti₃C₂ QDs serving as a photoelectrode matrix to enhance the PEC performance. Aptamer-based recognition was employed for the efficient capture of MC-LR molecules, enabling highly sensitive detection. The PC aptasensor exhibited a detection range of $5-50 \times 10^5$ pmol L⁻¹ and LOD of 17.4 pmol L^{-1} , while the PEC aptasensor achieved a detection range of $0.5-4 \times 10^5$ pmol L⁻¹ and LOD of 0.169 pmol L⁻¹ (Fig. 37b). This work established a foundation for the formulation of photoelectrode-centric PFC applications, significantly enhancing the scope for the establishment of highly sensitive PEC environmental analytical methodologies.

Phosphorescence, with its longer lifetime compared to fluorescence, is a relatively uncommon luminescent phenomenon. This unique characteristic allows the examination signal to successfully counteract the interference of the matrix autofluorescence and disseminated light. 226 ZnS QDs have attracted substantial interest and research emphasis with favorable phosphorescent emission characteristics, which are widely used as phosphorescent chemosensors for detecting pollutants in the living environment of plants. For example, a pioneering phosphorescent sensor was engineered utilizing a technologically advanced core-shell structure, Mn:ZnS QD@ZIF-8@MIP (chemosensor 138), for the highly sensitive and selective detection of CPF.²²⁶ Under the optimal operating parameters, 138 displayed the rapid detection of CPF within 5 min. It also exhibited a consistent, linear correlation over a concentration scope extending from 0 to 80 µM. Besides, the recoveries of CPF ranged from 92% to 105% in water samples with an LOD of 0.89 µM. This sensor combined the benefits of phosphorescent emission and molecular imprinting, significantly reducing the potential interferences from competing substances, scattered light, and background fluorescence. This innovation lays the foundation for the sensitive and selective detection of water pollutants using molecularly imprinted phosphorescent sensors.

Another study prepared a novel and highly fluorescent MOFbased host-guest hybrid system (ZnSQD@ZIF-67) for the detection of Cu2+ by incorporating polyethylene glycol (PEG)-coated ZnS QDs in ZIF-67 (chemosensor 139).227 The PEG-ZnS QD@ ZIF-67 nanohybrids combined the accumulation effect of ZIF-67 and ZnS QDs showed a highly selective and sensitive fluorescence response to specifically detect Cu2+. This allowed the detection of Cu²⁺, spanning a broad concentration range of 3-500 nM with an LOD of 0.96 nM (Fig. 37c). Compared to fluorescent sensors based on QDs without MOFs, nanohybrid 139 exhibited a significant enhancement in fluorescent QY. Therefore, ZnS QD-based sensors have shown substantial potential towards the comprehensive evaluation of the health and surroundings of plants.

However, although QDs have attracted significant attention due to their robust photobleaching stability, broad excitation range, and enhanced photostability, there are still some challenges that need to be addressed, as follows: (i) occasionally, it becomes imperative to modify QDs to enhance their stability and luminescent QY when coated within MOFs. Concurrently, the inclusion of an encapsulating agent during modification can efficaciously counteract the aggregation of QDs, although it may introduce complexities in the operational process. (ii) Inorganic semiconducting QDs routinely incorporate hazardous substances such as cadmium and lead, which can pose toxicity concerns when utilized for biological detection. (iii) Studies on QDs@MOF fluorescence chemosensors for biological detection are still lacking.

4.2.3 Organic dve@MOF-based fluorescent sensors. Fluorescent dyes have gained significant attention due to their low cost, easy availability, enhanced QY, robust optical attributes, and broad emission wavelength spectrum.204 However, although organic dyes offer luminous benefits, they are prone to aggregation, which lead to multi-chromophoric interactions that alter their color quality and suppress their fluorescence emission.²²⁸ In this case, encapsulating dyes in MOFs reduces their self-aggregation tendency. MOF materials possess adjustable skeleton structures and uniform pores, making them ideal for protecting fluorescent dyes and preventing fluorescence quenching due to aggregation. Furthermore, the interaction between dyes and MOFs allows the regulation of fluorescence properties.²⁰³ To date, the commonly used small-molecule fluorescent dyes including coumarins, doxorubicin and rhodamines have been integrated in MOFs to develop organic dye@MOF fluorescent chemosensors for the detection of pesticides, pH and metal ions.

Rhodamine B (RhB) is the most widely used fluorescent dye for constructing luminescent chemosensors to detect anions, cations and pesticide residues in the environment. For instance, a novel RhB@Zr-MOF composite exhibiting dualemission capabilities was developed (chemosensor 140).²²⁸ This unique construct was attributed to the interaction between the luminescent host Zr-MOF and the fluorescent guest RhB, enabling it to specifically recognize Fe3+ and nitenpyram. The introduction of RhB greatly improved the thermal stability, recyclability and low LOD (Fe3+ was 1.6 μM and nitenpyram was 0.2 µM) for sensing various analytes. Li et al. successfully Chem Soc Rev

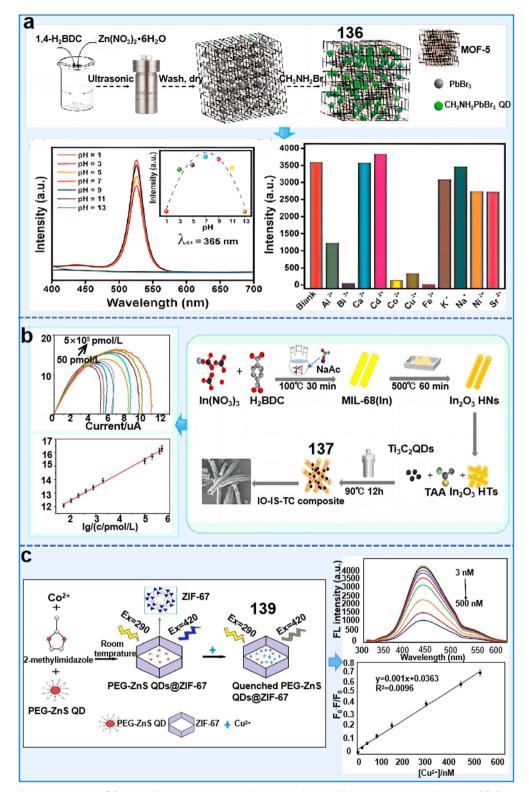


Fig. 37 Examples of quantum dot@MOF-based fluorescent sensors for monitoring the living environment of plants. (a) Emission intensities and selectivities of CH₃NH₃PbBr₃@MOF-5 composite for sensing various ions.²²⁴ Copyright © 2018, Elsevier. (b) Synthesis process of Ti₃C₂ QD@MOF chemosensor and its detection sensitivity for PEC.²²⁵ Copyright © 2022, ACS Appl. Mater. Interfaces. (c) Synthesis process of ZnSQDs@ZIF-67 and the detection sensitivity for CPF.²²⁷ Copyright © 2019, Elsevier.

designed a dual-emission fluorescent sensor by introducing RhB in the framework of HNU-48 (named RhB@HNU-48, chemosensor 141).229 The addition of RhB led to a significant improvement in the sensing sensitivity of alachlor, achieving an ultra-LOD of 0.59 ppb. This enhancement was due to the host-guest interactions, which influenced the excitation and emission spectra of the composite (Fig. 38a). This work was the first report on the use of a dual-emission fluorescence probe for

the detection of alachlor, and the detection capability of RhB@HNU-48 is higher than that of most sensors reported thus far. Furthermore, the practical application of this sensor was confirmed through its sensing performance in river and soil samples. This study created a logic gate using the sensing ability of RhB@HNU-48 to assess alachlor residue safety levels. Importantly, it presented a promising strategy for developing tailored sensors for agricultural residues. Li et al. developed an

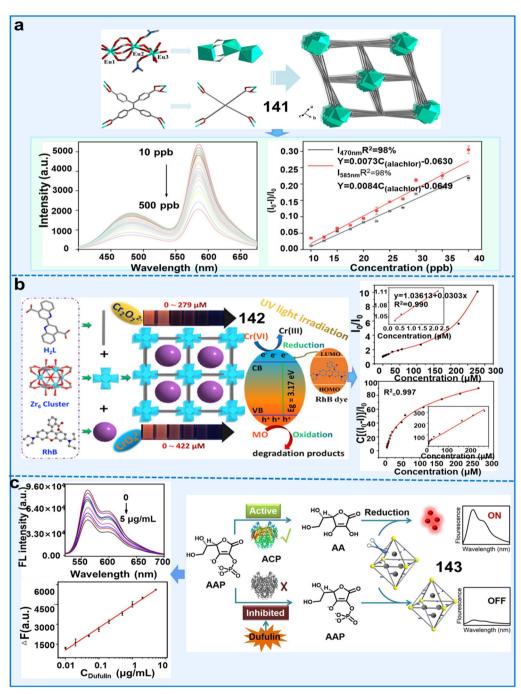


Fig. 38 Examples of organic dye@MOF-based fluorescent sensors for monitoring the living environment of plants. (a) Process for the synthesis of RhB@HNU-48 chemosensor and its detection sensitivity for alachlor.²²⁹ Copyright © 2022, ACS Appl. Mater. Interfaces. (b) Detection mechanism of RhB@Zr-MOF composites for sensing ions of $Cr_2O_7^{2-}$ and $CrO_4^{2-.230}$ Copyright © 2022, ACS Appl. Mater. Interfaces. (c) Process for the synthesis of DMOF chemosensor and its detection sensitivity for dufulin.²³¹ Copyright © 2022, Elsevier.

orange-vellow fluorescence sensor assembled by in situencapsulating rhodamine B (RhB) in a zirconium-biquinolinebased MOF (chemosensor 142).230 This approach effectively prevented the aggregation fluorescence quenching (ACQ) effect of RhB molecules within the RhB@Zr-MOF structure. The efficient electron transfer in RhB@Zr-MOF significantly enhanced its sensitivity in detecting Cr₂O₇²⁻ and CrO₄²⁻ ions, achieving ultra-LODs of 6.27 and 5.26 ppb, respectively. Compared to the pristine Zr-MOF, the sensitivity of RhB@Zr-MOF increased by approximately 6 and 9 times for Cr₂O₇²⁻ and CrO₄²⁻ ions, respectively (Fig. 38b). The aggregation fluorescence quenching (ACQ) effect of RhB molecules was effectively overcome. Importantly, RhB@Zr-MOF exhibited a rapid fluorescence quenching response toward Cr(v1) ions with high selectivity, sensitivity, and anti-interference resistance. This research offers a new approach for modulating the fluorescent detection sensitivity and photochemical removal efficiency for heavy metal ions and dyes. In addition to RhB, some other fluorescence dyes including coumarin, curcumin and doxorubicin have also attracted attention from researchers. The inclusion of 7-diethylamino-4-methyl coumarin (C460) within the pores of MOFs effectively mitigated the aggregation-induced quenching of dyes, without altering the original structure of the MOFs. For example, Liu et al. designed a dye-encapsulated zoterephthalate MOF-structured fluorescent chemosensor (143), specifically engineered for precise dufulin recognition.²³¹ 143 exhibited excellent sensitivity and linearity for the detection of dufulin and demonstrated a robust concentrationresponse relationship in the range of 0 to 5 µg mL⁻¹ with an LOD of 2.96 ng mL⁻¹ (Fig. 38c).

Importantly, 143 was successfully employed for examining the content of dufulin in cucumbers, polished rice, soil, and water. This investigation clearly demonstrated the practicality and untapped potential of MOF-derived nanosensors for detecting pesticides in the environment and food. Additionally, this work also opens up an avenue for the design of enzyme-based probes for pesticide sensing in environmental assessment and food safety. Zhong et al. synthesized a curcumin@MOF-5 composite via two methods (chemosensor 144),²³² which showed highly selective fluorescence enhancement responses to Al³⁺ with LODs of 3.10 µM and 2.84 µM for A-curcumin@MOF-5 and B-curcumin@MOF-5, respectively.

In conclusion, multiple fluorescent dyes have been used for the fluorescence detection recently; however, some limitations hinder their applications, as follows: (i) organic dyes frequently exhibit aggregation behavior, leading to a significant reduction in their luminescent intensity; (ii) the parameters including pH, temperature, and other substances modulate the fluorescent stability of organic dyes; and (iii) although introducing them in MOFs can improve their performance, studies on the detection of substances related to plant health are still lacking.

4.2.4 Metal nanocluster@COF-based fluorescent sensors. Metal nanoclusters (NCs) have recently attracted increasing attention because of their remarkable longevity, large Stokes shift, good photostability, and efficient electrocatalysis. In comparison to conventional fluorescent materials such as organic dyes and QDs, NCs are characterized with lower toxicity.245

However, their lower QY limits their further development. In this case, the incorporation of metal nanoclusters in MOFs to create composite materials effectively decreases aggregation and clustering, thereby enhancing their fluorescence detection ability and stability. At present, some metal ions including Ag, Au, Cu, and La have been encapsulated in MOFs to prepare metal cluster@MOF composites, which show great detection efficiency for metal ions and pesticides in the environment.

Among the above-mentioned metal nanoclusters, gold nanoclusters (AuNCs) have attracted tremendous interest owing to their distinctive properties and high application value in biosensing. For example, ZIF-8 was utilized to enwrap both CDs and gold nanoclusters (CDs/AuNCs@ZIF-8), subsequently producing an aggregate for the ratiometric fluorescence determination of Hg²⁺ (chemosensor 145).²³³ 145 enabled the highly sensitive detection of Hg2+, where the fluorescence intensity ratio (I_{640}/I_{440}) exhibited a distinct decreasing trend with an increase in the concentration of Hg²⁺ in the concentration range of 3 to 30 nM, achieving an LOD of 1 nM. In another study, AuNCs were synthesized within a Zr-MOF (AuNCs@UiO-66) for monitoring the concentration of Hg2+ in water (chemosensor 146).²³⁴ This nanocomposite exhibited exceptional sensitivity for detecting Hg2+ in real water samples, achieving an LOD of 193 pM. Compared with the above-mentioned chemosensor, this composite showed higher detection sensitivity. 146 with stable and high fluorescence could be easily fabricated using a simple method. Its properties make it valuable not only for detecting various metal ions but also for applications in the field of biology. Additionally, Cai et al. successfully constructed a dual-signal chemosensor of AuNCs@ZIF-8 for the detection of organophosphorus pesticides (chemosensor 147).²³⁵ 147 exhibited strong fluorescence with a fluorescence lifetime and QY of 6.83 µs and 4.63%, respectively. The MOF carrier restricted the molecular mobility of AuNCs, leading to the manifestation of the AIE effect. As a result, the composite exhibited a robust fluorescence signal, characterized by a fluorescence lifetime of 6.83 µs and QY of 4.63%. In addition, an innovative smartphone application (app) was designed to ensure real-time monitoring of pesticide contamination. The gray values of the solution were determined using a smart phone app, subsequently yielding calculated recoveries of OPs in the range of 85.2% to 113.8% (Fig. 39a). Compared to conventional single-signal biosensors, this chemosensor exhibited higher sensitivity and reliability. The reasons for this improvement are as follows: (1) encapsulating AuNCs with an AIE effect into ZIF-8 restricts their molecular movement and amplifies their fluorescence signal. (2) By inhibiting the enzymatic hydrolysis product, H2O2, using the decomposition effect of H₂O₂ on ZIF-8 and the peroxidase mimic activity of AuNCs, a dual signal detection is achieved through fluorescence and color changes. Furthermore, a colorimetric test paper was developed for the visual detection of OPs. Additionally, the gray values of the solution were obtained using a smartphone app for the on-site quantitative detection of OPs with an LOD of 0.4 μ g L⁻¹.

This method exhibited higher sensitivity and reliability compared to traditional single-signal biosensors. Besides

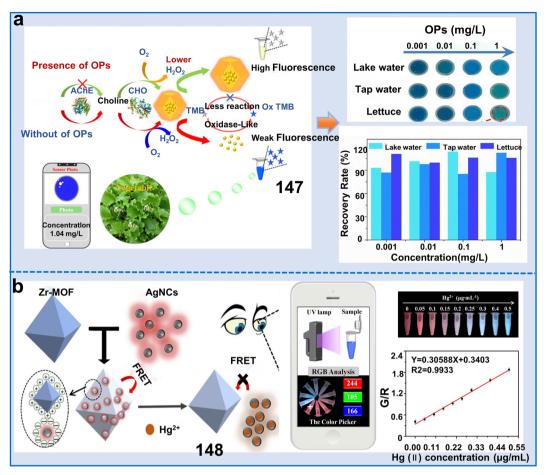


Fig. 39 Application of metal nanocluster@COF-based sensors for monitoring the living environment of plants. (a) Schematic diagram of the synthesis of AuNCs@ZIF-8 and the mechanism for the detection of OPs. 235 Copyright (©) 2022, ACS Appl. Mater. Interfaces. (b) Schematic diagram of the synthesis of Zr-MOF sensor and its mechanism for the detection of Hg²⁺.²³⁶ Copyright © 2022, Elsevier.

AuCNs, AgNCs, CuNCs and LaNCs have also gained attention for fluorescence imaging. For instance, a dual-emission ratiometric fluorescence chemosensor (148) based on Zr-MOF and AgNCs was constructed for the accurate and intuitive detection of Hg²⁺. ²³⁶ Upon exposure to Hg²⁺, the AgNCs in the chemosensor underwent aggregation, causing a decrease in fluorescence. In contrast, the fluorescence intensity exhibited by Zr-MOFs demonstrated a slight increase because of the diminished FRET interaction between AgNCs and Zr-MOFs. This sensor demonstrated excellent sensitivity in the concentration range of 0.010 to 0.5 μg mL⁻¹, achieving an LOD of 1.8 μg L⁻¹ (Fig. 39b). This simple, fast, and highly sensitive fluorescence probe provides a promising approach for assessing the safety of food contaminated with Hg²⁺. Another study synthesized a new dual-emission fluorescent sensor (chemosensor 149) CuNCs@ Tb@UiO-66-(COOH)₂ for the detection of Cu²⁺.²³⁷ The fluorescence ratio and Cu²⁺ concentration showed a good linear relationship when fitted in the range of 1-30 μM, with an LOD of 178 nM. This study offers a novel approach to design multifunctional ratiometric fluorescent sensors using a one-pot method with MOFs as support materials. Abdelhamid et al. synthesized a series of new isostructural lanthanide-based

MOFs based on the trimolecular linker of 2,4,6-tri-p-carboxyphenyl pyridine (H₃L₂), together with La³⁺ as their select metal cluster (chemosensor 150).²³⁸ The fluorescence emission intensity exhibited a linear decrease in the concentration range of Fe³⁺ from 16.6 to 167 μM, and the Stern-Volmer analysis further verified linearity and revealed an LOD of 16.6 μM. This study introduced a novel platform with potential applications in biosensing. Therefore, NC-based fluorescent sensors possess great efficiency and performance for the detection of metal ions and pesticide residues, but only a few types of metal ions has been reported for designing fluorescent sensors currently. Moreover, further endeavors are necessary to enhance the sensitivity and selectivity of materials for improved performance in future applications.

4.2.5 Perovskite@MOF fluorescent sensors. Perovskite materials have attracted increasing attention due to their advantageous characteristics, including high QY, tunable optical properties and low cost. However, the stability of hybrid perovskites remains a concern given that it can lead to their degradation, affecting their long-term performance. Accordingly, they can be combined with some relatively stable MOFs for the construction of robust perovskite@MOF assemblies that

exhibit enhanced chemical stability and luminescence.241 Besides, by integrating dopant-modified perovskites within MOFs, it is feasible to fabricate ratiometric fluorescent sensors boasting diverse emission profiles as a result of the distinctive PL of these two substances.²³⁹ In the past few years, CsPbBr₃, MAPbBr₃, and CH₃NH₃PbBr₃ have been doped in MOFs for the construction of fluorescence chemosensors. However, their applications in monitoring the health and surrounding of plants are still lacking.

Recently, only one study reported the function of perovskite@MOFs for the identification of substantial heavy metal ions. Subsequently, this research disclosed an innovative methodology that was pioneering in incorporating bisected inorganic perovskite nanocrystalline components in lanthanide MOFs, which constructed a ratiometric fluorescent chemosensor (151) for the determination of Hg²⁺ in aquatic medium (Fig. 40).²³⁹ 151, consisting of CsPbBr₃@Eu-BTC, exhibited exceptional stability and fluorescence output in water. When exposed to Hg²⁺, the fluorescence of CsPbBr₃ emitting at 520 nm was instantaneously depleted via an electronic transfer mechanism. However, the red emission from Eu-BTC peaking at 616 nm remained unaffected. Meantime, this color change was easily observed by the naked eye, providing a visual indication of the existence of Hg²⁺. The CsPbBr₃@Eu-BTC fluorescent chemosensor could rapidly, sensitively and selectively detect Hg2+ and exhibited a linear concentration range of 0 to 1 µM and impressive LOD of 0.116 nM. Therefore, introducing perovskites in MOFs effectively improves the analytical proficiency of MOF-based sensors, but studies on the design and application of perovskite-based MOF fluorescent sensors are still lacking.

In summary, the application of perovskite-containing MOF materials for fluorescence sensing is still somewhat restricted owing to a few key challenges, as follows: (i) the strategies for combining and incorporating perovskite nanocrystals with luminescent MOFs are still complex and not fully understood and (ii) the primary obstacle hindering the practical sensing applications of perovskite@MOF fluorescent sensors in water is their poor fluorescence and water stability.

4.3 Covalent organic frameworks (COFs)

COFs have become attractive materials for fluorescence sensing due to their high fluorescence QY, extendable framework, and excellent chemostability and thermostability. 246 The luminescence properties of COFs are determined by the presence of abundant π -conjugation structures within their skeleton, which are created through a broad array of chemical bindings and affinities resulting from the unique monomer constituents of the material. The diverse functional groups in COFs as chromophores also have potential to promote their luminous efficiency.²⁴⁷ Nevertheless, the poor intrinsic conductivity and weak electrocatalysis of most COFs obviously limit their application. Thus, to amplify the sensitivity of COF-based materials, various desirable modifications have been implemented, including metal encapsulation, incorporation of carbon-based nanomaterials, and the fabrication of COF composites with other porous nanostructures.²⁴⁸ According to previous reports, COF-based fluorescent sensors have made great achievements in detecting pesticide residues, anions and cations in the living environment of plants (Fig. 41). In the following parts, we elaborate the applications of functional COFbased fluorescent chemosensors including various linkage types of COFs and COF-based composites in the detection of plant-related aspects (Table 9).

4.3.1 Specific linkage types of COFs for fluorescence detection. Different connection units forming various types of functional COFs with outstanding characteristics and great application potential in fluorescence detection have been widely studied. Comprehending and pinpointing the fundamental components and linkage systems present in COFs have opened the path to engineering materials with specifically customized attributes suitable for distinct applications. 254 At present, COFs

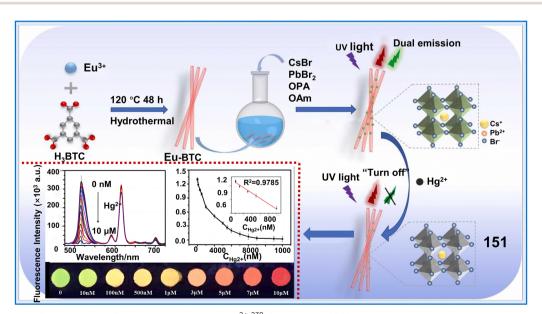


Fig. 40 Application of CsPbBr₃@Eu-BTC for the visualization of Hg^{2+, 239} Copyright © 2022, Elsevier.

Review Article

وesticide residue sensing Liezine-type and hydrazone **Functional** s-based sensors Hg²⁺ Metal ion sensing Cu²⁺ al ions@COFs based composite LOCs of plant

Fig. 41 Classification of functional COF-based sensors and their application in the detection of pesticide residues, metal ions and plant disease monitoring.

based on Schiff base, triazine and hydrazone groups and other types such as sp² carbon-conjugated COFs have been used for the detection of pollutants in the living environment of plants.

Imine-type COFs, known as "Schiff bases", are synthesized through an esterification response between aldehydes and amines.248 This reaction leads to the formation of the Schiff base functionality (-C=N-), which is characteristic of imine linkages in the COF structure. This chemical union imparts noticeably high stability and robustness to the ensuing framework, presenting imine-type COFs with potential usage in the detection of pesticides and metal ions.

For example, a luminescence sensor was engineered by fabricating a novel imine-bonded conjugated COF (IC-COF) through the reaction between 2,4,6-tris(4-formylphenoxy)-1,3,5triazine and 1,5-diaminonaphthalene (chemosensor 152). 152 demonstrated remarkable selectivity towards PO₄³⁻ and an LOD of 0.61 µM (Fig. 42).249 Furthermore, the exceptional recycling capability of IC-COF display substantial potential for reutilization without a discernible degradation in performance (5.2% decrease post 5 recycling cycles). The persistent issue with imine-based COFs is the propensity for nonradiative transition in response to π - π stacking interactions, giving rise to the aggregation-caused quenching (ACQ) effect. This triggered a

reduction or complete cessation of COF luminescence emission.²⁵⁰ Thus, to solve this problem, Song et al. synthesized an electrochemical luminescent material with properties to mitigate the ACQ event. Subsequently, they synthesized an imine-linked COF (TFPPy-TPh-COF) with high electrochemiluminescence (ECL) emission and the capability of eliminating the ACQ effect and further constructed an ECL sensor for the detection of malathion (chemosensor 153). The efficient quenching of ECL was achieved by electrochemiluminescence resonance energy transfer (ERET) from the excited state of TFPPy-TPh-COF to zeolite imidazolate framework-8 (ZIF-8) and the steric hindrance of ZIF-8. 153 exhibited an extremely low LOD of 2.44 pg mL⁻¹ together with a broad dynamic concentration range of 0.01 to 1000 ng mL⁻¹. It could be effectively employed for the detection of other OPs (e.g., paraoxon, methidathion, and chlorpyrifos) and utilized for the measurement of malathion in apples, lettuce, and pakchoi. This research offers a new opportunity for the synthesis of ECL materials with high performance and the development of new ECL sensors for the detection of various pesticides.

Besides, triazine-type and hydrazone-linked COFs possess several remarkable properties such as chemical stability, good thermal stability, and high nitrogen content. These properties make them promising for various applications, particularly fluorescence detection in the study of plant-environment interactions. For Chem Soc Rev

 Table 9
 The application of COF-based fluorescent sensors in monitoring the living environment of plants

Classifications	Chemosensors Name	Name	Response range	Response range Limit of detection (LOD)	Target analytes	Applications	Ref.
Special linkage types 152	152	IC-COF	ı	0.610 µM	PO_4^{3-}	Detection of PO ₄ ³⁻ in water	249
of COFs	153	TFPPy-TPh-COF	$0.01-1000 \text{ ng mL}^{-1} 2.44 \text{ pg mL}^{-1}$	$2.44 \mathrm{~pg~mL}^{-1}$	Malathion	Monitoring the concentration of malathion in	250
	ļ		5		7	pakchoi, lettuce, and apples	i
	154	Triazine-COF	0.1-10 µM	96.0 nM	Glyphosate	Detecting the distribution of glyphosate in	251
						water and soil	
	155	Bth-Dma COF	0-100 µM	0.170 µM	Fe ³⁺	Monitoring the concentration of Fe3+ in water	252
	156	sp ² -carbon-linked COF	0-150 µM	1.43 µM	Cu^{2+}	Monitoring the concentration of Cu ²⁺ in water	253
	157	Bpy-sp ² c-COF	0-20 nM	Hg^{2+} : 2.42 nM, Ni^{2+} : 2.73 nM,	$Hg^{2+}, Ni^{2+}, Cu^{2+}, Co^{+}$	Hg ²⁺ : 2.42 nM, Ni ²⁺ : 2.73 nM, Hg ²⁺ , Ni ²⁺ , Cu ²⁺ , Co ⁺ Detection of various ions including Hg ²⁺ , Ni ²⁺ ,	254
				Cu ²⁺ : 1.47 nM, Co ⁺ : 2.20 nM		Cu ²⁺ , and Co ⁺ in water	
COF-based composite 158	158	AuNPs@COF	$10-800 \text{ ng mL}^{-1}$	$0.610~ m ng~mL^{-1}$	OPs	Monitoring the concentration of OPs in food	255
fluorescent sensors						and water	
	159	MnO_2 @COF	1	$0.0632 \text{ and } 0.108 \text{ ng mL}^{-1}$	Chlorpyrifos	Detecting the residue of chlorpyrifos in water	256
				by two treatments		and vegetables	
	160	CDs@TDCOFs@PNIPAM	$5-400 \text{ µg L}^{-1}$	$4.88 \ \mu g \ L^{-1}$	Pyrethroids	Monitoring the pyrethroids concentration in	257
						cabbage, cauliflower, and apple	
	161	CDs@COF	10 – $100~{ m \mu g~L}^{-1}$	$0.750~\mathrm{\mu g~L^{-1}}$	Hg^{2+}	Detection of Hg ²⁺ in water	258
	162	Dve/MOFs@COFs	$0.1-1 \text{ mg L}^{-1}$	2	VÕCS	Monitoring the VOCs from wheat scab	259

example, a study constructed a triazine-COF-derived electrochemical chemosensor (154), which was designed to facilitate specific non-covalent interactions with glyphosate (GLY) for detecting GLY.²⁵¹ 154 exhibited a wide linear operation range of 0.1 µM to 10 µM of glyphosate and demonstrated an LOD of 96 nM and a limit of quantification (LOQ) of 320 nM. This work shows significant potential for further improvements and commercialization as a versatile disposable sensing platform specifically designed for the detection of glyphosate in water and fruits. Chen et al. designed and successfully synthesized two stable crystalline hydrazone-linked COFs containing functional O,N,O'-chelating sites by Schiff-base condensation reactions (chemosensor 155) (Fig. 43).²⁵² The as-synthesized Bth-Dma COF exhibited strong fluorescence in both the solid state and aqueous suspension and demonstrated exceptional sensitivity for detecting Fe³⁺ in water with an LOD of 0.17 μM. The recognition process can be attributed to the coordination interaction with Fe³⁺. This groundbreaking study introduced the first instance of utilizing a robust luminescent COF material with pre-designed O,N,O'-chelating sites for the detection of Fe³⁺. This research may lay the foundation for developing luminescent COF sensors with targeted binding sites to detect specific metal ions. Therefore, triazine-type and hydrazone-linked COFs have shown great efficiency for the detection of ions and pesticides in the environment, but related studies on their applications in the monitoring of the health and environment of plants are still lacking.

Additionally, COFs with sp²-carbon chains exhibited commendable photoelectric attributes that make them effective in the fields of luminescent material production and chemical detection systems. Notable, they have been harnessed for plant habitat monitoring purposes also. For instance, Yan et al. constructed an AIE-active unit-containing and sp²-carbon-linked COF (chemosensor 156).²⁵³ The conjugated backbone of sp²-TPE-COF, interlinked by olefinic bonds, functioned as a highly informative sensor for detecting metal ions. 156 significantly improved the dispersion of COFs and finely modulated their sensitivity towards Cu2+, resulting in a remarkably increased Stern-Volmer constant (K_{sv}) value of 15.15 \times 10⁴ m⁻¹ (Fig. 44a). The present investigation underscored the considerable promise inherent in employing surfactant-modulated, extensively π -conjugated COFs for sensor technology applications. This work can open up opportunities for creating more fully conjugated COFs to detect a wider range of water-soluble toxic analytes. Zhu et al. reported a fully π -conjugated COF with dual binding sites, Bpy-sp²c-COF, which demonstrated commendably swift fluorescence recognition and substantially amplified adsorption tendencies toward divalent heavy metal ions (chemosensor 157) (Fig. 44b).²⁵⁴ XPS analysis confirmed the concurrent coordination between metal ions and both cyano and bipyridine groups in Bpy-sp²c-COF, leading to its efficient fluorescence recognition and adsorption capabilities for Cu²⁺, Hg^{2+} , Ni^{2+} and Co^{2+} . The fully π -conjugated COF, demonstrating dual ligand binding sites, offered a promising and innovative method for formulating sensors possessing exceptional attributes. At present, exploration into robustly π -conjugated COFs for fluorescent sensing and contaminant remediation remain

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470 nm 153 H₂O/DMSO (160:0.5ml Cat. aq. AcOH 80 °C/5 day

Fig. 42 Precipitation methodology for IC-COF and the influence of phosphate ions on its fluorescence properties. 249 Copyright © 2023, the American Chemical Society

Intense fluorescence

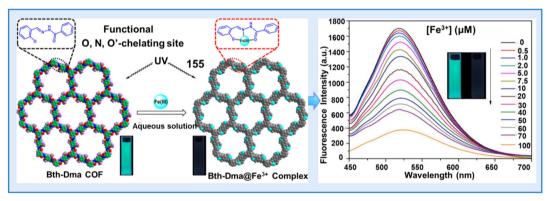


Fig. 43 Schematic illustration of the designed synthesis of Bth-Dha and Bth-Dma COFs, as well as their functional O,N,O'-chelating sites. 252 Copyright © 2019, the American Chemical Society.

scarce, primarily owing to their intricate synthetic procedures, which typically result in relatively modest success rates. Thus, further efforts should be focused on sp2 c-COFs and their versatile applications.

4.3.2 COF-based composite fluorescent sensors. Metal nanoparticles (MNPs) have gained significant attention recently due to their exceptional catalytic attributes. Unfortunately, the aggregation of MNPs (e.g., AuNPs, PtNPs, and PdNPs) is a common issue due to their high surface energy, resulting in decreased catalytic efficiency and difficulties in their extended storage. Research indicates that by leveraging the expansive porous structures and remarkable stability of COFs, there have been successful efforts to combine MNPs such as AuNPs,

PtNPs, and PdNPs with COFs. COF-MNP composites offer the synergistic benefits of the excellent catalytic activity of MNPs and the unique advantages of COFs, and can be utilized for detecting pollutants in plants and their surrounding environment.260 For example, Li et al. developed a novel coreshell nanocomposite, PB@Fe-COF@Au, for the highly efficient detection of OP residues (chemosensor 158) (Fig. 45a). 255 The PB nanoparticle (PBNP) cores with Fe2+ and Fe3+ exhibited peroxidase-like activity, while metallated porphyrins and AuNPs also acted as peroxidase-mimicking catalytic sites. Therefore, PB@Fe-COF@Au possessed satisfactory triplet peroxidase-like catalytic efficiency (Fig. 45a). The use of the triple nanozyme enhanced the sensitivity of the sensor and effectively reduced

Non- fluorescent

Chem Soc Rev

a 156 Liquid N₂ & Ultrasound Knoevenagel Exfoliation condensation sp2-TPE-COF Nanosheets Electron transfer process Copper ion detection -0 222 V Cu²⁺/Cu⁴ 1.368 V Fluorescence sensing Heavy Metal ions 157 Adsorption capacity Removal Recyclable Stable Detectable R²=0.995 Intensity (a.u.) (F₀-F)/F

Fig. 44 Application of sp²-carbon-linked COFs for monitoring the living environment of plants. (a) Synthesis of sp²-TPE-COF, copper ion detection, and its electron transfer process during copper ion sensing with sp²-TPE-COF.²⁵³ Copyright © 2022 Wiley-VCH GmbH. (b) Schematic illustration of Bpy-sp² c-COF for the detection and removal of divalent heavy metal ions.²⁵⁴ Copyright © 2022, Elsevier.

700

Wavelength (nm)

0.0

1×10-8

Hg2+ (M)

interference in the detection of OP. In comparison to previous studies, this sensor achieved a broader linear range (10-800 ng mL⁻¹) and a lower detection limit (0.61 ng mL⁻¹) for chlorpyrifos. These improvements were directly linked to the synergistic interplay among the triple catalytic sites of PB@Fe-COF@Au, which also functioned as its triple responsive sites for OPs. This research offers a novel approach for the design and application of efficient nanozymes for on-site monitoring of pesticides.

Besides, metal oxide MnO₂ NPs have also been introduced in COFs to improve their catalytic efficiency due to their expansive

surface area, substantial adsorptive potential and superior biocompatibility. For example, Wen et al. developed a cuttingedge COF/methylene blue@MnO2 (COF/MB@MnO2) composite, which demonstrated superior signal amplification, a unique binding entity, and robust oxidase-mimicking activity (chemosensor 159).²⁵⁶ In the absence of OPs, the MnO₂ coating on the surface could detect thiocholine (TCh) due to the enzymatic breakdown of acetylthiocholine (ATCh), catalyzed by acetylcholinesterase (AChE). The inhibitory activity of OPs against AChE and their impact on the generation of TCh

2×10-8

provided the basis for the accurate detection of chlorpyrifos. The detection could be achieved through complementary electrochemical and photothermal measurements, with LODs of 0.0632 ng mL⁻¹ and 0.108 ng mL⁻¹, respectively. Moreover, this sensor demonstrated exceptional selectivity and robust anti-interference capability for the precise detection of chlorpyrifos in diverse environmental and biological samples, effectively distinguishing it from interfering substances (Fig. 45b). This study offered a dual-mode detection method for OPs that is convenient and suitable for on-site testing in various scenarios. Additionally, it broadened the practical utilization range of COF-derived multifunctional composites for application in multimodal sensing systems. Therefore, introducing metal oxides into MOFs is another effective strategy to improve the detection efficiency.

COFs employed together with carbon nanomaterials can avoid the lack of electron conductivity. However, only a few

studies reported the combination of CDs in COFs to detect pesticide residues and heavy metal ions in the environment. CDs, as quasi-spherical fluorescent nanoparticles based on carbon, possess excellent chemical stability, abundant low-cost sources, and strong resistance. These attributes make them highly promising for selective detection applications. However, the nanoscale size of CDs leads to intrinsic self-aggregation, resulting in the quenching of AIE. 257 Therefore, to prevent self-aggregation, a viable and intelligent approach is to encapsulate CDs within the channels or pores of COFs. For example, Zhang et al. created a fluorescent composite called CDs@TDCOFs@PNIPAM by encapsulating CDs within 1,3,5-tris(4-formylphenyl)benzene (TFB)/2,5dihydroxyterephthalohydrazide grafted with thermally responsive poly(N-isopropylacrylamide) (PNIPAM) (CDs@TDCOFs@PNIPAM, chemosensor 160) (Fig. 46).²⁵⁷ 160 demonstrated a temperaturereactive "on/off" detection module for pyrethroids through

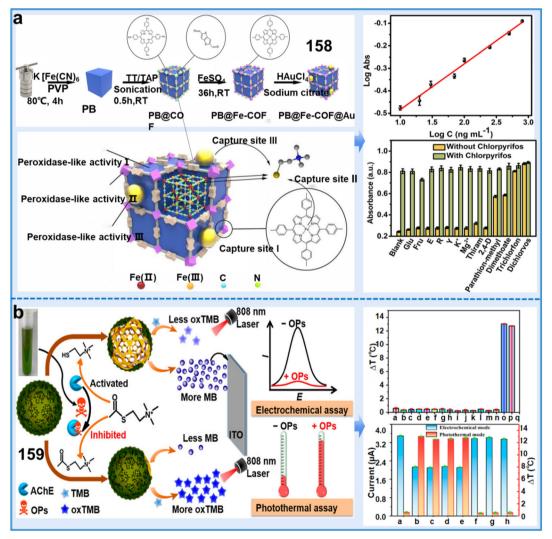


Fig. 45 Fluorescence sensors based on metal and metal oxide NP composites for the detection of OPs in the environment. (a) Synthesis of PB@Fe-COF@Au composite and its diagrammatic sketch of triplet peroxidase-like active sites and multiple capture sites.²⁵⁵ Copyright © 2023, the American Chemical Society. (b) Synthesis of the COF/MB@MnO2 composite and its detection mechanism, selectivity and anti-interference capacity of OPs (from a to p: blank, Fe^{2+} , Fe^{3+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Hg^{2+} , As^{5+} , glucose, methionine, arginine, glycine, citric acid, thiamine nitrate, chlorpyrifos, and a mixture of all the above-mentioned substances, respectively). ²⁵⁶ Copyright © 2023, the American Chemical Society.

target-catalyzed electron exchange. The model manifested an expansive linear measurement range of 5 to 400 μg L⁻¹ with an LOD of 0.69 μg L⁻¹. Concurrently, CDs@TDCOFs@PNIPAM, equipped with red, green, and blue (RGB) fluorescent emissions, was combined with a smartphone-assisted apparatus, facilitating the visually discernible and astute quantification analysis of pyrethroids, exhibiting an LOD of 4.875 $\mu g L^{-1}$ (Fig. 46). Another study designed and synthesized an innovative composite of imine-bonded COF doped with CDs for the analytical monitoring of Hg2+ in environmental water (chemosensor 161), which exhibited superior sensitivity and discriminative fluorescence response to low concentrations of Hg2+ in water. 258 The analytical threshold of the sensor was in the range of 10 to 100 μ g L⁻¹, presenting an LOD of 0.75 μ g L⁻¹. This costeffective and simple-to-construct fluorescent COF offers promising prospects for the precise detection and efficient removal of diverse pollutants present in irrigation water.

MOFs are traditionally known as a family of structurally aligned substances affiliated with COFs, exhibiting comparable essential characteristics to COFs such as high surface area, tunable accessibility and extended crystalline structure. COFs possess strong covalent linkages, which endow them with the exceptional thermal and chemical stability vital for chemical detection under harsh conditions.²⁶¹ Integrating MOFs with COFs presents a promising strategy to elevate the performance and expand the application scope of COFs. 260 Currently, only one study reported an MOF@COF composite as a chemical fluorescence sensor to detect the substances related to plant health. Furthermore, the practical application of colorimetric sensor arrays still face challenges, including environmental humidity interference and insufficient sensitivity towards minute traces of target volatile organic compounds (VOCs).²⁵⁹ Thus, to address these challenges, Wang et al. developed a solution by creating dye/MOF@COF core-shell composites via the application of hydrophobic COF overlayers on top of MOFs loaded with dyes (chemosensor 162).²⁵⁹ The composite-based sensor, benefiting from the uniform dispersion of dyes across the porous MOF structure, exhibited enhanced sensitivity at sub-ppm levels for the detection of VOCs compared to conventional dye sensors. The developed dye/UiO@TPB-DVA-COF composites exhibited excellent sensing capabilities for the differentiation and detection of eight plant VOCs.

This array facilitated the precise and timely detection of wheat scab, even as early as one day after inoculation (Fig. 47). This study suggested that MOF@COF composites offer a versatile platform for constructing colorimetric sensing arrays exhibiting exceptional humidity sensing capabilities and robustness. These arrays hold significant promise for practical application scenarios, particularly in monitoring the health of plants.

In summary, although considerable achievements have been made in the development of COF-based sensors, the synthesis of COFs and their composite counterparts encounters significant hurdles, as follows: (i) the exorbitant expense associated with precursor materials, together with the ecological risks posed by these substances and the organic solvents utilized throughout the process pose significant obstacles in their largescale industrial production; (ii) enhancing the operational duration and performance of COF-modified electrodes is crucial, and there is a pressing need to develop materials that offer high loading efficiency and excellent conductivity; (iii) further

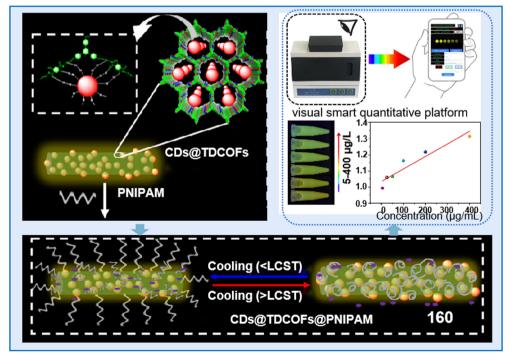


Fig. 46 Process for the synthesis of CD@TDCOF@PNIPAM composite and CD@TDCOF@PNIPAM-based smartphone readout analysis of LCY in real samples. 257 Copyright © 2022, the American Chemical Society

Review Article Dye adsorption COFs growth Released VOCs 162 Color differential maps of eight VOCs

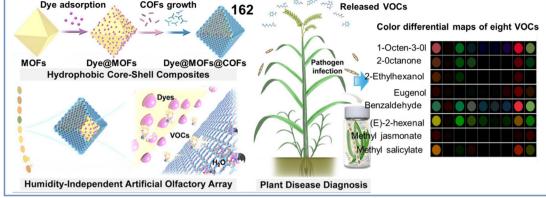


Fig. 47 Schematic diagram of the synthesis of dye/MOF@COF core-shell composite and the detection of the released VOCs by pathogens for the diagnosis of diseases in plants.²⁵⁹ Copyright © 2022, the American Chemical Society.

innovation is required in the methods and means of functionalizing COFs; and (iv) their application range is still limited, especially in the field of monitoring plant health. Thus, designing COFs with better biocompatibility and adaptability is imperative to further expand the application scope of electrochemical sensors.

4.4 Nanoclusters

Nanoclusters (NCs), typically consisting of a single or multimetal core with a diameter of less than 2-3 nm, have attracted significant attention due to their broad Stokes shifts, very intense fluorescence bands, good biocompatibility and strong PL.²⁶² Additionally, NCs are known for their simple preparation and low toxicity, making them a preferred choice compared to other fluorescent materials such as toxic QDs and organic dyes.²⁶³ Nanoclusters can be categorized into single metallic clusters and bimetallic clusters based on the composition of species within their cores.²⁶² Thus far, these NC-based fluorescent sensors have been widely used for monitoring the living environment of plants (Fig. 48). Here, we introduce the applications of single NCs, bimetallic NCs and NC-based fluorescent chemosensors in the above-mentioned aspects in detail (Table 10).

4.4.1 Single metal NC-based sensors. Metal nanoclusters (MNCs) consist of a few to several hundred metal atoms, exhibiting discrete energy levels because of their nanoscale size. This characteristic gives rise to exceptional optical properties in MNCs. Besides, MNCs possess attractive properties such as ultra-small size, excellent biocompatibility, and outstanding photostability, making them an ideal choice for fluorescent materials.²⁶⁸ Among the various types of MCNs, AuNCs, CuNCs and AgNCs are the most widely used MCNs for developing fluorescent sensors. In the following parts, we elaborate the applications of these three single NCs in monitoring the living environment of plants.

Gold nanoclusters (AuNCs), an exclusive subset of metallic NCs, demonstrate a marked Stokes shift, adjustable emission response, and commendable biosafety, which are emerging as a cutting-edge subclass of fluorescent materials for developing high-performance sensors.²⁷⁸ Fluorescent AuNCs have been

successfully employed for the identification of various pollutants, including pesticide residues and metal ions in the living environment of plants. For example, Li et al. synthesized hydrolysateresponse disulfide bond-functionalized gold nanoclusters (S-S-AuNCs, chemosensor 163).205 Remarkably, S-S-AuNCs exhibited a distinct response to low pH values and thiol compounds, enabling their application as highly efficient sensors for organophosphates (OPs). This sensing mechanism relied on the AChE-facilitated hydrolysis of acetylthiocholine in thiocholine and CH₃COOH, with OPs inhibiting the activity of AChE (Fig. 49a). In addition, S-S-AuNCs were implemented for the meticulous examination of the distribution, residue and metabolization of methidathion within pakchoi. Another study also developed a novel dual-signal fluorescent sensor for detecting OPs in vegetables based on GSHsynthesized AuNCs (GSH-AuNCs, chemosensor 164).264 164 is based on the catalytic activities of acetylcholinesterase (AChE) and choline oxidase (ChOx), which convert acetylcholine (ACh) into choline and generate hydrogen peroxide (H2O2). This process leads to increased cyan fluorescence due to aggregation. Besides a mobile application called "RGB Color Picker" was employed to visually detect organophosphates (OPs) by recognizing the RGB values of fluorescent colors associated with different OP concentrations. This sensor exhibited a linear dynamic range of 10-2000 ng mL⁻¹ with a detection limit of 2.05 ng mL⁻¹. This sensor demonstrated the ability to detect a wide range of organophosphates (OPs), but it lacked specificity in distinguishing individual types of OPs.

Besides the detection of pesticides, several studies reported that AuNCs can also detect metal ions in the environment. For instance, Zhang et al. developed a simple fluorescent chemosensor (165) using a single AuNC chemosensor for the rapid discrimination of heavy metal ions (HMIs).265 165 was synthesized by chemically reducing the gold precursor, HAuCl₄, using 2-mercapto-1-methylimidazole (MMI) in the presence of polyvinylpyrrolidone (PVP). The resulting PVP/MMI-AuNC exhibited significant responsiveness towards diverse metal ions. This resulted in a distinctive fluorescent response at both wavelengths of 512 nm and 700 nm (Fig. 49b). The observed changes in fluorescence could serve as a unique fingerprint, enabling

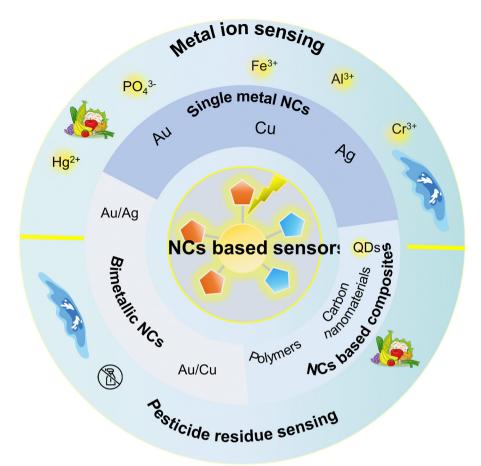


Fig. 48 Classification and applications of NC-based sensors in plant-related environment monitoring.

the accurate discrimination of metal ions. By utilizing this newly developed PVP/MMI-AuNC-based fluorescent sensor array as our primary receptor, we could detect and unequivocally identify numerous heavy metals such as Ag⁺, Fe³⁺, Fe²⁺, Mn²⁺, Sn²⁺, Pb²⁺, and Hg²⁺. Hada et al. achieved the successful synthesis of photoluminescent His-AuNCs, enabling the quantification of hazardous levels of Fe²⁺ in low-volume samples (chemosensor 166). 266 Importantly, it exhibited high selectivity and accuracy for detecting Fe²⁺, achieving an LOD of 3.2 μM. Finally, the realized transportable sensor was ascertained for its functionality in authentically assessing the Fe²⁺ levels in water samples that had been spiked with 35 μ M Fe²⁺. This portable sensing platform could monitor the concentration of heavy metals in water samples. Hence, AuNC-based sensors exhibit excellent selectivity and accuracy for detecting ions and pesticides in the environment and can monitor their toxicity level in the real environment.

In addition to AuNCs, CuNCs and AgNCs also have very intense fluorescence signals, which have been applied in the field of fluorescence detection. ²⁷⁹ For example, Xu *et al.* developed the first CuNC-based fluorescent sensor array (chemosensor **167**) to identify 12 metal ions (Pb²⁺, Fe³⁺, Cu²⁺, Cd²⁺, Cr³⁺, Co²⁺, Ni²⁺, Zn²⁺, Ag⁺, Fe²⁺, Hg²⁺, and Al³⁺) and various organic compounds, such as humic substances, lipids, fatty acids, amino acids, and lignans. ²⁶⁷ These 12 metal ions could be detected at a

concentration limit of 1.5 µM. Furthermore, the developed method allowed for the quantification of metal ions even at a low concentration of 0.83 μM (Zn²⁺) (Fig. 49c). This constitutes the pioneering fluorescent sensor array constructed with CuNCs for the sensitive detection of various metal ions in water. The array was also employed to distinguish seawater and riverine samples from various regions, showcasing its potential for water quality evaluation. Chen et al. accomplished the development of a dual-emission nanocomposite using His-AgNCs for the detection of Cu²⁺ (chemosensor 168).²⁶⁸ It showed high detection sensitivity, good selectivity and anti-interference, and LOD of 0.4 ppm. In addition, this work designed a polymer film to load a dual-emission nanochemosensor, which meant that the visual detection of Cu²⁺ is possible. This work indicates the potential application prospects of dual-emission fluorescent nanochemosensors in the analysis of the living environment of plants.²⁶⁹

4.4.2 Bimetallic NC-based sensors. Bimetallic NCs have attracted great attention in the past few years due to their better catalytic activity, strong luminescence and higher sensitivity due to the synergistic effect of two types of metal atoms.²⁷¹ Thus far, bimetallic NC-based fluorescent sensors including Au/Ag, Au/Cu and bimetallic composite NCs have been used for the monitoring of the living environment of plants. Here, we introduce the application of these bimetallic NC-based chemosensors in this field.

Table 10 The applications of NC-based fluorescent sensors in the detection of pollutants in the living environment of plants

Classifications	Name	Chemosensors	Chemosensors Response range	Limit of detection (LOD)	Target analytes	Applications	Ref.
Single NC-based Au NCs sensors	Au NCs	163 164	0.05 -20 ng mL $^{-1}$ 10-2000 ng mL $^{-1}$	$0.0150~{ m ng~mL^{-1}}$ 2.05 ng mL $^{-1}$	Methidathion OPs	Detecting the methidathion residue in foods Monitoring the concentration of OPs in	205 264
		165		17.0 nM for ${ m Ag}^{\scriptscriptstyle +}$	${ m Ag}^+_{-}, { m Fe}^{3+}, { m Fe}^{2+}, { m Mn}^{2+}, { m Sn}^{2+}, { m Pb}^{2+}$	Ag^+ , Fe^{3+} , Fe^{2+} , Mn^{2+} , Sn^{2+} , Detection of metal ions in water Pb^{2+} , and Hg^{2+}	265
	Cu NCs	166 167	Sn~: 0.100–10.0 μМ 	3.20 µМ 1.50 µМ	Fe ²⁺ , Fe ³⁺ , Cu ²⁺ , Cd ²⁺ , Cr ³⁺ , Co ²⁺ , Ni ²⁺ , Zn ²⁺ , Ag ⁺ , Fe ²⁺ , Ta ²⁺ , Ag ⁺ , Fe ²⁺ , Ta ²⁺ , Ag ⁺ , Fe ²⁺ , Ta ²⁺ , Ag ²⁺ , Fe ²⁺ , Ta ²⁺ , Ta ²⁺ , Ag ²⁺ , Fe ²⁺ , Ta ²⁺ , T	Fe ²⁺ Pb ²⁺ , Fe ³⁺ , Cu ²⁺ , Cd ²⁺ , Cr ³⁺ , Detection of Fe ²⁺ in water $C0^{2+}$, Ni ²⁺ , Zn ²⁺ , Ag ⁴⁺ , Fe ²⁺ , Detection of 12 metal ions in water $C0^{2+}$, Ni ²⁺ , Zn ²⁺ , Ag ⁴⁺ , Fe ²⁺ ,	266 267
	Ag NCs	168	0–10 ppm 0–3.0 µМ	$0.400~{ m mg~L}^{-1}$ 21.0 nM	and Al 10sate	Monitoring the concentration of Cu^{2+} in foods Detecting the glyphosate residue in lettuce and A. thaliana	268 269
Bimetallic based Au/Cu NCs sensors	Au/Cu NCs	169 170	50 nM-1 mM Two linear range of 5.0 \times 10 ⁻⁷ –7.0 \times 10 ⁻⁶ M and 7 0 \times 10 ⁻⁶ 10 \times 10 ⁻⁴ M	10.0 nM 0.100 µМ	Cr^{3+} Fe^{3+}	Detection of Cr^{3+} in water Detection of Fe^{3+} in water	270 271
		171	Hg^{2+} : 0-50 μM	2.45 nM for Hg^{2+} ,	Hg ²⁺ and Cu ²⁺	Monitoring the distribution of Hg^{2^+} and Cu^{2^+} in 272 water and food	272
NC-based composite-based sensors	CQDs@CuNCs N-GQDs	172	or thiram, r paraquat mol $L^{-1} \times$ mol $L^{-1} \times$	7.49 nM for thiram, Thiram and p 3.03 nM for paraquat 4.12×10^{-9} mol L^{-1} for Cu^{2+} and Cd^{2+} Cu^{2+} Cu	araquat	Detecting the occurrence and concentration of thiram and paraquat in water Monitoring the concentration changes of Cu^{2+} and Cd^{2+} in food	268
	Blue-emitting CDs 174			5.00 nM for Cu^{2+} ,	Cu^{2+} and Hg^{2+}	Monitoring Cu^{2+} and Hg^{2+} in water	274
	WS ₂ -QDs AuNC@nanogel	175 176	$0.3 \text{ to } 3 \text{ Le}_{2000 \text{ HM}}$ 0.3 to 3 μM 0.625 to 125 ng mL ⁻¹	$^{\prime}$.00 that left rig 0.120 $\mu{ m M}$ 0.590 ng mL $^{-1}$	Cu ²⁺ Chlorpyrifos	Detection of Cu^{2+} in water Monitoring the concentration of chlorpyrifos in food	275 276
	BiNCs@AB	177	$3.0 \text{ ng L}^{-1} \text{ to } 1.0 \text{ mg L}^{-1}$	$1.00~\rm ng~L^{-1}$	Pb^{2+}	Detection of Pb^{2+} in water	277

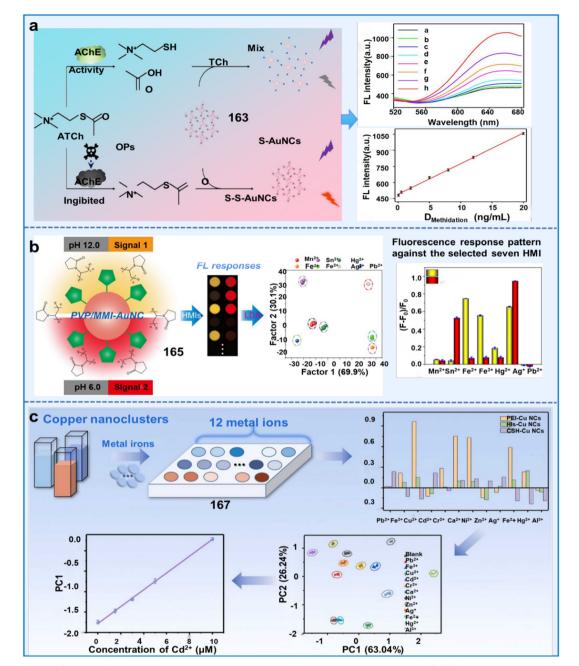
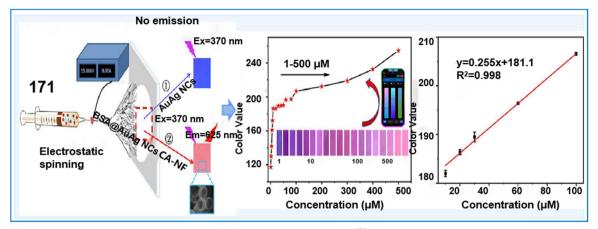


Fig. 49 Single-metal NCs based fluorescent sensors used for monitoring the living environment of plants. (a) Sensing mechanism and application of S-S-AuNCs for detecting OPs. 205 Copyright © 2021, the American Chemical Society. (b) Schematic illustration of the CuNC-based fluorescent sensor array for detecting different metal ions. 265 Copyright © 2022, Elsevier. (c) Schematic representation of the PVP/MMI-AuNC-based fluorescent sensing system for identifying various HMIs.²⁶⁷ Copyright © 2021, Elsevier.

Au-based bimetallic NCs are widely utilized for the detection of metal ions in soil and irrigation water. For example, Nie et al. prepared highly luminescent Cu/Au bimetallic nanoclusters (BNCs) by employing GSH for not only the reduction process but also as an enveloping shield, thus circumventing the aggregation of the synthesized nanoclusters (chemosensor 169).²⁷⁰ When excited at 380 nm, Cu/Au BNCs showed an emission peak at 450 nm. Selective quenching of Cu/Au BNCs by Cr³⁺ facilitated the implementation of an analytical approach benefiting from their broad linear dynamic range of 50 nM to 1 mM and superior sensitivity (LOD = 10 nM, S/N = 3). Shojaeifard et al. utilized the remarkable metallophilicity and PL properties of Au and Cu clusters to design a chemosensor based on bimetallic goldcopper nanoclusters (PA-AuCu bi-MNCs, 170).²⁷¹ The fluorescence intensity of PA-AuCu bi-MNCs was selectively quenched in the presence of Fe³⁺, resulting in the hindrance of their emission. This work demonstrated an LOD of 0.1 µM and highlighted the independence from most interferences, making it an important feature of the study. Therefore, compared to single NCs, Au-based bimetallic NCs show high selectivity and anti-interference.



Schematic illustration of the fabrication of AuAg-ENM and its sensing process.²⁷² Copyright © 2023, Elsevier

Additionally, using other materials for the immobilization of bimetallic NCs has gained great attention due to their improved fluorescence performance for the trace identification of metal ions and pesticides in food and water. For example, Wu et al. synthesized a ratiometric fluorescent system (chemosensor 171) by integrating AuAgNCs within electrospun cellulose acetate nanofibrous membranes (ENM). This strategy enabled the facile, rapid and visual detection of both Cu^{2+} and Hg^{2+} in Petri dishes under diverse conditions.²⁷² It was successfully utilized for detecting amino acid L-histidine (His) sequentially, a pivotal stem that integrated His analysis with a smartphone platform for quantitative on-site monitoring. This sensor exhibited exceptional performance in detecting traces of Hg²⁺ and Cu²⁺, with LODs of 12.36 nM and 25.90 nM, respectively. The high selectivity of the AuAg-ENM system further enhanced its capability for monitoring and controlling the safety standard of Hg²⁺ and Cu²⁺ in multiple applications (Fig. 50). This developed system was validated using real environmental water samples, demonstrating its practicality for on-site detection using a smartphone with convenient operation.

4.4.3 NC-based composite-based sensors. To overcome the inherent tendency of MCNs to aggregate, incorporating diverse ligands/templates in NCs to form NC-based composites has been proven effective to greatly enhance their fluorescence properties, sensitivity and stability towards metal ions.²⁶³ At present, various ligands including QDs, carbon nanomaterials, polymers and other porous materials have been used to stabilize MNCs, which show great detection efficiency for metal ions and pesticides in the environment.

QDs have been introduced in NC sensors to improve their detection efficiency and sensitivity through their exceptional optical attributes, robust photochemical stability, prolonged fluorescence lifetime, low toxicity, and stable emission. For example, a ratiometric fluorescent sensing system (chemosensor 172) was constructed by leveraging red-emitted CuNC complexes and blue-radiating N-CQDs to effectively assess the concentrations of thiram and paraquat with LODs of 7.49 nM and 3.03 nM, respectively (Fig. 51a).269 At the same time, the ratiometric fluorescence probe achieved satisfactory recovery

results, ranging from 82% to 114%, for actual food measurements. More interestingly, thiram and paraquat could be swiftly and visually detected via a smartphone-enabled colorimetric evaluation, offering an efficient methodology for the real-time monitoring of pesticide residues in fruits. Another study constructed a ratiometric fluorescence nanomixture of GQDs-AuNCs specifically for the quantitative analysis of Cu²⁺ and Cd²⁺ in fruits (chemosensor 173).²⁷³ Under the optimal conditions, the fluorescence intensity ratio (I_{565}/I_{403}) of the GQD-AuNC system showed a linear relationship with the concentration of Cu²⁺ or Cd²⁺ in the range of $8 \times 10^{-8} \text{ M} - 6 \times 10^{-6} \text{ M}$ and $1 \times 10^{-6} \text{ M} - 4 \times 10^{-5} \text{ M}$, respectively. Also, its detection limits were 4.12×10^{-9} M and 9.43×10^{-7} M, respectively. When Cu^{2+} and Cd^{2+} were present, the paper-based visual sensor exhibited detectable fluorescent color changes, enabling rapid on-site detection. The findings suggest that the ratiometric fluorescence sensor holds great significance in food safety and biological analysis. Babaee et al. designed an innovative dual-emissive ratiometric nanohybrid chemosensor comprised of red-emitting (Ag/Au)@insulin NCs and blue-emitting CDs for the sensitive and selective ratiometric determination of Hg²⁺ and Cu²⁺ (chemosensor 174).²⁷⁴ The LODs for the determination of Cu²⁺ and Hg²⁺ were estimated to be 5 nM and 7 nM, respectively. Interestingly, the selectivity of this probe towards these two ions could be easily controlled by adjusting the pH of the probe solution without requiring any chelating agents. This unique feature allowed the selective detection of Cu²⁺ and Cd²⁺ ions by simply modifying the pH of the probe solution without the need for any additional reagents. Another study introduced a ratiometric fluorescent nanosensor (NCs/QDs, chemosensor 175) for the detection of Cu²⁺ ions by combining the stable optical properties of AuAgNCs and WS2-QDs.²⁷⁵ The addition of WS2-QDs could avoid the interference from Pb²⁺ and Cd²⁺ in the process of detecting Cu²⁺ due to their advantages of simple synthesis and stable luminescence properties. This sensor exhibits significant potential for detecting Cu²⁺ in river samples, offering great application potential in practical environmental monitoring. Therefore, QD-based NCs can achieve the fast and visual detection of ions and pesticides in the environment.

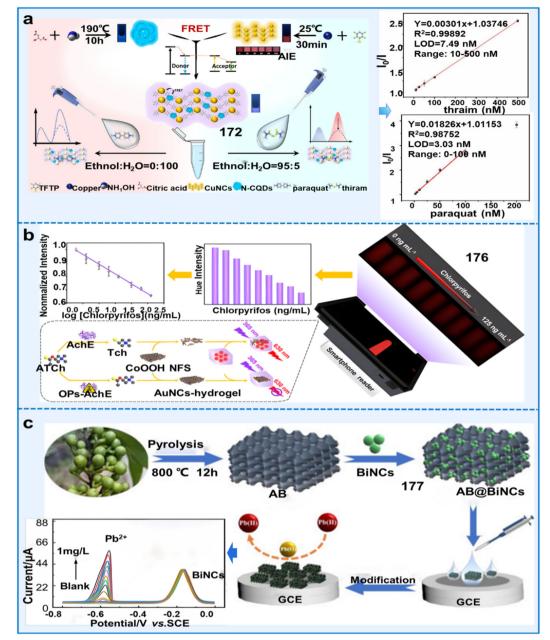


Fig. 51 Applications of NC-based composite-based fluorescent sensors in monitoring the living environment of plants. (a) Schematic representation of the ratiometric fluorescent sensor for the detection of pesticides using N-CQDs@CuNCs.²⁶⁸ Copyright © 2023, Elsevier. (b) Schematic illustration of the portable fluorescent hydrogel test kit for the on-site quantitation of chlorpyrifos. 276 Copyright © 2021, the American Chemical Society. (c) Process for the fabrication of the BiNC@AB composite sensor for the sensing of Pb^{2+, 277} Copyright © 2021 The Authors. Published by the American Chemical Society

Hydrogels, as stable 3D networks with environmentally friendly properties, have gained considerable interest for immobilization and encapsulation purposes in sensor technology. Hydrogels, serving as water-holding networks, offer nanometer-scale porous structures that enable the passage of small molecules by providing physical encapsulation to trap nanoparticles.²⁷⁶ The effective integration of the excellent performance of hydrogels with NCs can greatly enhance the accuracy and stability of sensors. For example, Wang et al. developed a portable handheld platform integrated with smartphones for the on-site detection of OPs (chemosensor 176).276 Cobalt oxyhydroxide nanoflakes (CoOOH NFs) could effectively suppress the fluorescence originating from AuNC hydrogel systems through the FRET effect (Fig. 51b). By converting the fluorescent colors into digital information by using self-made auxiliary devices and smartphones, the on-site monitoring of the concentration of chlorpyrifos was achieved with an LOD of 0.59 ng mL⁻¹. This sensor presented good selectivity, antiinterference, high sensitivity and capability due to the encapsulation of the hydrogel into specific AuNC signatures in practical analysis, offering huge potential for on-site applications.

Besides, a highly porous activated biochar (AB), exhibiting superior electrical conductivity, extensive surface area, and robust chemical stability, was selected as a support material to assist NCs in enhancing their excellent conductivity and electrocatalytic efficiencies. As demonstrated by Zou et al., a ratiometric electrochemical chemosensor (177) was constructed using the BiNC@AB-modified electrode to analyze Pb²⁺.²⁷⁷ BiNCs were capable of not only forming an alloy with Pb2+ to enhance the affinity of Pb2+ towards the electrode interface, but also generating reference signals crucial in the precise and accurate process of electrochemical detection using a ratiometric approach (Fig. 51c). The prepared sensor exhibited an excellent electrocatalytic performance towards Pb²⁺, with a satisfactory linear range and detection limit, which was attributed to the synergistic effect of these advantages. Therefore, AB as the support material can greatly improve the detection efficiency of NCs, but related studies are still limited.

In conclusion, despite the significant progress in the development of nanoclusters, many hurdles persist when advancing and endorsing the practical utilization of COFs for electrochemical analysis. (i) Reports regarding the utilization of metal nanoclusters as sensors for detecting Na⁺, K⁺, and Ca²⁺ ions are rare, mainly because of the suboptimal binding affinity displayed by the core of metal nanoclusters towards these ions; (ii) controlling the size regulation of nanoclusters remains challenging with the aim to enhance their photochemical attributes such as quantum efficiency and mitigate the complexities associated with post-synthesis purification tasks;280 (iii) the incomplete understanding of the internal assembly process involved in metal nanocluster synthesis, thereby exacerbating the intricacy associated with enhancing their photochemical attributes; (iv) primary utilization of nanoclusters typically occurs within water samples, as opposed to plant samples where further detection utilities still exist and demand exploration in this field.

5. Applications of fluorescent supramolecular chemosensors

To provide accurate information for managing plant health, fluorescent supramolecular chemosensors with the advantages of recyclability, high sensitivity, selectivity and adaptability are suitable for a wide range of on-site environments.²⁸¹ To date, there are two types of fluorescent supramolecular materials, polymers and hydrogels, which are excellent tools for monitoring the health and living environment of plants (pesticides, ions and plant components). In the following section, we summarize and analyze the application of fluorescent supramolecular chemosensors in these aspects.

5.1 Polymer systems

Fluorescent polymers are specific due to the properties of their fluorophores such as photovoltaic properties and non-covalent bonding that stimulate reactivity and reversibility.²⁸² The non-covalent linkages affect the luminous characteristics of chromophores given that they have the ability to control the aggregation states and energy transfer through assemblydisassembly processes.²⁸³ Utilizing a variety of structures, polymer sensors have been widely used for various analytes, such as pesticides, metals, and toxins (Table 11). In the following sections, we discuss the application of conjugated fluorescent polymers, organometallic polymers, and molecularly imprinted polymers for monitoring the above-mentioned analytes (Fig. 52).

5.1.1 Conjugated fluorescent polymers. Conjugated polymers are compounds that form high molecular weight compounds consisting of one or more π - π * conjugated electronic structural unit linked by covalent bonds. The conjugated structure of conjugated fluorescent polymers allows the free flow of electrons/energy throughout their structure, and the light energy captured by each monomer can be delivered as a collection, producing a fluorescent signal multiplication effect. Some research groups have reported the use of conjugated fluorescent polymers for the detection of pesticides in water and the development of polymer test papers for the visual detection of pesticides in a recyclable manner. In one example, an article reported a carbazole-containing polymer (PAN-Cs, chemosensor 178) that could incorporate six pesticides (isopropalin, trifluralin, fenitrothion, glyphosate, cyfluothrin, and imidacloprid) in its porous structure for detecting these pesticides. Among the pesticides, trifluralin was the best at quenching the fluorescence of 178, with a pronounced fluorescence-quenching response could be seen for the determination of trifluralin both in water and on a test paper prepared from the polymer. Furthermore, the test paper could be recycled 12 times and still retained its original detection function (Fig. 53a).²⁸⁴ The results indicated that 178 can recognize multiple pesticides and its specificity should be improved by adding specific recognition units or utilizing different reaction mechanisms. Another illustrious instance of the utilization of fluorescence for the identification of detrimental pesticides is fluorescent microporous polyamines (PAN-Ls, chemosensor 179) with suspended dibromotriphenylamine and triphenylamine chromophore groups, which could also bind three pesticides (trifluralin, fenitrothion, and glyphosate) in their porous structure. The PAN-L-Br chemosensor exhibited higher sensitivity to the pesticide molecules and the chemosensing test papers prepared with the polymers to test for fenitrothion, possessed a quick and sensitive fluorescence quenching reaction, and could be recycled 10 times. The pore size of 179 showed a positive correlation with the sensitivity detection of pesticides, owing to the fact that the larger size can increase the interaction of pesticides with recognition groups (Fig. 53b).²⁸⁵ However, although these studies demonstrated that paper coated with chemosensors is an efficient, rapid and promising method for the detection of pesticide residues, studies are still lacking on measuring the pesticide residues in real samples.

To realize the detection of pesticide residues in water resources, farmland and agricultural products, researchers have developed a variety of pesticide sensors. One paper reported a fluorescent sensor combining fluorescent conjugated polymer

 Table 11
 The applications of polymer system-based fluorescent sensors for monitoring the health and environment of plants

Classifications Chemosensors Name	Chemosenso	rs Name	$\lambda_{\rm ex}/\lambda_{\rm em}~{ m (nm)}$	Solvents	Limit of detection (LOD)	Target analytes	Applications	Ref.
Conjugated fluorescent polymers	178	PAN-Cs	365/467–500	Aqueous solutions	0.350 µМ	Trifluralin, isopropalin, glyphosate, fenitrothion, imidacloprid, and	Detecting six different pesticides in water 284	r 284
	179	PAN-Ls	365/479-490	Ethanol	0.100 mM	cynuotinni Fenitrothion, trifluralin	Detection for three pesticides in water	285
	180	FCPNPs-MnO ₂	470/536	Phosphate buffer (PB, 10	$1.12~\mathrm{pg~mL}^{-1}$	and gypnosate Carbaryl	Detecting Carbaryl by fluorescence	286
	181	nanosneets Su-TPE/PrS	320/470	Tris-buffer (20 mM, pH =	500 μМ	Paraoxon methyl	quenciums Detection of paraoxon methyl in farm- land or motor	287
	182	UCNPs-GNPs	099/086	Acetone-phosphate buffer $(0.2 \text{ mmol } 1.^{-1} \text{ mir} - 6.5)$	1.42 nM	Malathion	Detection of malathion in water and tea	1 288
	183	rGO-TPP	414/649, 717	$V_{\rm DMF}:V_{\rm methanol}=1:1$	27.7 fM	Cd ²⁺	Monitoring the concentration of Cd ²⁺ in	1 289
Organome- tallic polymers	184 185		293/617 377/590, 615	Methanol Hexane	0.800 µM —	Fipronil Triethyl phosphate	water Monitoring fipronil in water Detecting triethyl phosphate in solution	290
	186	CFP-Sm-CeO ₂ -	310/350, 615	Tris-HCl buffer solution (5 mmol L^{-1} , pH = 8.0)	1.00 μМ	Methyl parathion	and gas states Detection of methyl paraoxon in Chinese herbal plants (Poria cocos and semen	292
	187	Cd-CBCD	390/467	Dimethylacetamide	145 ppb	2,6-Dichloro-4-nitroaniline	Detecting DCN in water	293
	188	LCP 1	345/405	THF Aqueous solution	1.15 μ M 3.83 μ M for Fe ²⁺ , 2.33 μ M for Hg ²⁺ , 1.97 μ M for Fe ³⁺ ,	(DCA) Ee^{2+}	Detection of DCN in water Detecting Fe ³⁺ . Fe ²⁺ , Hg ²⁺ , and Fe ³⁺ in river water	294
						Hg ²⁺ Fe ³⁺		
	189	I	324/462	Aqueous solution	0.360 µM 0.590 µM	DCN Fe ³⁺	Detection of the pesticide DCN in water Detection of the Fe ³⁺ in water	295
Molecularly/ ion imprinted	190 191	— Microfluidic paper chip (paper@QDs@	365/484 395/528, 640	Aqueous solution NR	1.02 ppm 90.0 nM	Fe ³⁺ 2,4-Dichlorophenoxyacetic acid (2,4-D)	Detection of Fe $^{3+}$ in river water samples Detecting 2,4-D in soybean sprout and lake water	296 297
polymers	192	Molecularly imprinted 450-470/525 membrane chroma-	450-470/525	NR	$20.0~\mathrm{\mu g~mL}^{-1}$	Triazophos	Detecting the concentration of triazophos in water	298
	193	ography surp AgNPs-MIP films sensor	365/420	Na-phosphate buffer (20 mM, pH = 6.0, containing	$0.300~\mathrm{ng~mL}^{-1}$	Aflatoxin B1	Detecting the distribution and concentration of AFB1 in maize flour	299
	194	ARS-MIP	469/560	Phosphate buffer (20 mM, $pH = 8.5$)	0.100-100 µМ	Cu^{2+}	Detecting Cu ²⁺ in water.	300
	195	CQDs@Cu-IIP	343/448	Aqueous solution	$0.0160~{ m mg}~{ m L}^{-1}$	Cu^{2+}	Detecting Cu ²⁺ in river water	301
Other special	196 197 198	Cu(n)-FIIS Pb(n)-IIP FD@ALB	438/493 395/430 370/505, 575	Double-distilled water Pure water PBS $(1 \text{ mM, pH} = 7.4)$	0.140 μM 2.10 μg L ⁻¹ 0.570 μM	Cu ²⁺ Pb ²⁺ Chlorpyrifos	Detecting Cu ²⁺ in river water Detecting Pb ²⁺ in different water samples Detection of CPF in	302 s 303 304
polymers	199	HN-Chitosan-3	440/555	Deionized water containing 0.1 M hydrochloric acid	1.66 μМ	НСНО	boot, water, and som Detecting HCHO in water samples	305

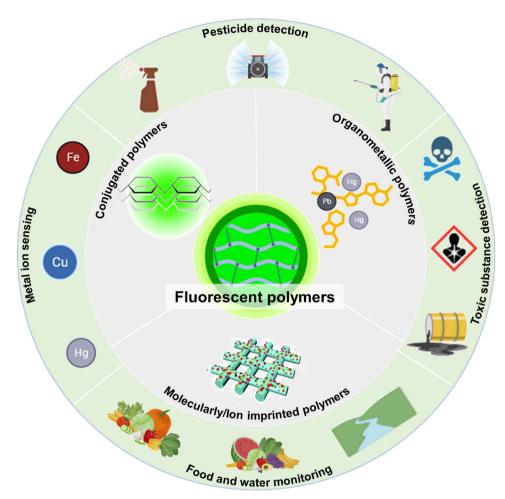


Fig. 52 Application of fluorescent polymers for monitoring the living environments of plants and food safety. Mainly divided into pesticide residue detection, soil environment heavy metal testing and fruit safety aspects of the test.

nanoparticles (FCPNPs) (chemosensor 180) with manganese oxide (MnO₂) nanosheets, and then the fluorescence of 180 could be quenched by the MnO₂ nanosheets. AChE could induce the disruption of MnO2 nanosheets, and then result in the recovery of the fluorescence of FCPNPs. To restrict the recovery of the fluorescence signals, we could limit the destruction of MnO₂ nanosheets through the inhibition of AChE activity via carbaryl (Fig. 53c). 180 showed good linear concentration responses in the range of 5-300 pg mL⁻¹ with an LOD of 1.02 $\mu U\ mL^{-1}.$ The "off-on" property increased the sensitivity and accuracy of 180 for monitoring the effect of pesticides on AchE activity.²⁸⁶ Researchers also developed a polymerization-induced emission (AIE)-based sensor (181) assembled by electrostatic interaction between a cationic polyelectrolyte protamine (PrS) and tetra-anionic sulphonyl derivative of tetraphenylethylene (Su-TPE). The supramolecular complex disintegrated as a result of the enzyme degradation of PrS in the presence of trypsin, and the enzymatic activity of trypsin was significantly inhibited by the pesticide methyl paraoxon, thus restoring the fluorescent signals of the Su-TPE/PrS polymers (Fig. 53d). 181 showed a good linear concentration range of 0 nM to 16 nM with an LOD of 0.22 nM.²⁸⁷ The results implied that the use of 181 was an effective method

for the quantitative detection of organophosphorus in agricultural fields or water resources by monitoring enzymatic activity. In another conjugated polymer (chemosensor 182) for the detection of pesticides assembled by electrostatic interactions, to produce FRET, negatively charged upconversion fluorescent nanoparticles (UCNPs) were combined with cationic conjugated polymer-encapsulated gold nanoparticles (GNPs), and the fluorescence intensity decreased linearly with an increase in malathion concentration from 0.01 to 1 μM with an LOD of 1.42 nM (Fig. 53e). However, the fluorescence quenching of 182 may increase false positives in the detection of pesticides, which implies that the polymerization mechanism of 182 should be improved.288 These studies have successfully designed fluorescent sensors for monitoring a variety of pesticides, and further studies should focus on developing novel detection kits for measuring enzymatic activity or pesticide concentration.

In addition to detecting pesticides, conjugated fluorescent polymer sensors were designed to detect heavy metal ions in water. One study employed noncovalent-coupled 5,10,15,20tetraphenylporphyrin-reduced graphene oxide (rGO-TPP) to create a sensor (chemosensor 183), which could detect Cd²⁺ with high sensitivity and without interference. The detection

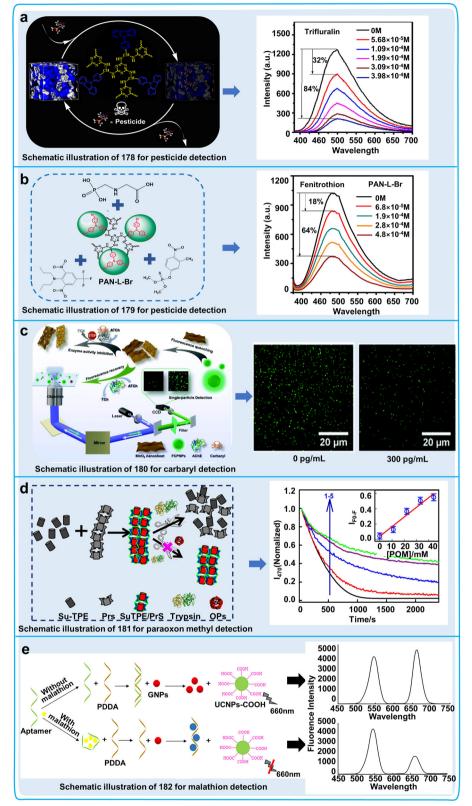


Fig. 53 Detection process, data graphs and practical application diagrams of conjugated fluorescent polymers for the detection of pesticides. (a) Detection mechanism and spectra of different concentrations of pesticides (trifluralin as an example) in water by 178.²⁸⁴ Copyright © 2020, the American Chemical Society. (b) Schematic and spectra of 179 for the detection of different concentrations of pesticides (fenitrothion as an example). ²⁸⁵ Copyright © 2018, the American Chemical Society. (c) Schematic representation of the detection of the pesticide carbaryl by 180 and fluorescence images of FCPNPs detecting different concentrations of carbaryl. Reproduced from ref. 286 with permission from The Royal Society of Chemistry. ²⁸⁶ Copyright © 2019, The Royal Society of Chemistry. (d) Schematic representation of the 181 assay for methyl paraoxon and a plot of data on the inhibition of trypsin activity as measured by the fluorescence decay of the 181 complex at different concentrations of methyl paraoxon. ²⁸⁷ Copyright © 2021, Elsevier. (e) Schematic and fluorescence spectra of malathion detection by 182. ²⁸⁸ Copyright © 2020, Elsevier.

behavior of 183 was examined for 20 significant metal ions, and only Cd2+ was found to enhance the non-fluorescent rGO-TPP sensor to resume fluorescence. Cd2+-induced fluorescence turnon of the analyte was observed in the response range from micromolar to femtomolar, and the system was found to be the most sensitive Cd²⁺ sensor to date at the lowest experimentally detectable concentration of 3.86 fM (Fig. 54). Ultimately, rGO-TPP was also created as a solid-phase filter paper sensor that may be employed in on-site Cd²⁺ monitoring applications.²⁸⁹ In terms of convenience and applicability, the rGO-TPP filter paper sensor is an effective tool for detecting metal ions in practice, but its application scope should be improved.

Currently, conjugated fluorescent polymers are commonly used to identify pesticides and ions in the living environment of plants. To improve the application scope of these sensors, some challenges should be solved. (i) We should focus on the development of "off-on" conjugated fluorescent polymers that can improve the detection accuracy and sensitivity. (ii) Further studies should focus on the detection of more stable conjugated fluorescent polymers or combined with a smartphone for increasing their application in a variety of practical environments. (iii) The complex synthesis process and difficult purification of conjugated fluorescent polymers limit their wide application.

5.1.2 Organometallic polymers. The family of crystalline organic-inorganic materials known as metal coordination polymers is made up of organic linkers and metal ions or clusters with well-defined structures, tunable pore sizes, and inherent crystallinity. Metal coordination polymers have been used to

trace pesticide residues in water and in Chinese herbs. One example was the first use of a europium metal coordination polymer (chemosensor 184) for detecting fipronil (Fig. 55a), which had no impact on the luminescence of the fipronil-quenched polymers in the presence of other common pesticides. 184 showed a good linear concentration range of 10⁻⁶ to 10⁻⁴ M with an LOD of 0.8 µM. This is the first time that metal-organic coordination polymers were established for detecting pesticides and further studies should focus on developing a europium metal polymer test paper to facilitate the detection of fipronil in real samples.²⁹⁰ Besides, another similar europium-containing metal supramolecular polymer was used to recognize pesticide mimics. 4-Oxy-2,6-bis-(1'-methylbenzimidazolyl)pyridine-containing amphiphilic end-capped poly(tetrahydrofuran) supramolecular polymeric films (chemosensor 185), consisting of different ratios of Eu³⁺ and Zn²⁺, exhibited a significant optical response in the presence of triethyl phosphate, a mimic of organophosphorus pesticides (Fig. 55b). With an increase in temperature, 185 showed greater sensitivity for detecting triethyl phosphate, implying that it has high potential for monitoring temperature and chemicals.²⁹¹ In another example of supramolecular polymers, fluorescent chemosensor 186 with cerium-based fluorescent polymers (CFP) and samarium-doped cerium oxide composites (Sm-CeO2), depolymerization of the supramolecular structure and fluorescence quenching were induced by para-nitrophenol (p-NP) generated by hydrolysis of methyl parathion (MP) by Sm-CeO₂, which in turn was used for the detection of the pesticide methyl parathion in Chinese herbal plants (Poria cocos and Semen coicis) (Fig. 55c).²⁹² Although the use of metal coordination polymers

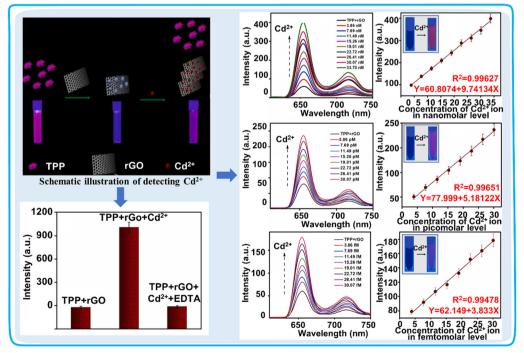


Fig. 54 Schematic of the detection of Cd²⁺ by the 183 sensor, statistical plot of the competitive interaction in the presence of different molecules and quantitative fluorescence detection spectra of Cd²⁺ concentration (nanomolar, picomolar and femtomolar concentrations) by 183.²⁸⁹ Copyright © 2023, Elsevier.

Chem Soc Rev

2500 a -2500 (n.e) -1500 -1000 -500 Intensity (8 600 620 640 660 680 700 720 Wavelength (nm) Ksv: 9.33×103M-1 2.0 Detection limit: 8×10⁻⁷M 1.8 1.6 5 1.2 1.0 0.00 0.02 0.04 0.06 0.08 0.10 Fiproni Wavelength (nm) b Triethyl phosphate **Triethyl Triethyl** phosphate vapour phosphate in hexane Neat film 185 Solution Intensity/a.u. vapour Ditopic ligand endcapped macromonomer 185 and the formation of a metallo-supramolecular polymer 450 500 550 600 650 λ (nm) C 25000 20000 intensity 15000 10000 교 5000 186 400 500 Wavelength (nm) 1.0 0.8 0.6 0.4 v=46.74x+193.45

Fig. 55 Detection process, data graphs and practical application diagrams of organometallic fluorescent polymers for the detection of pesticides. (a) Spectrograms and Stern–Volmer plots of **184** for the detection of different concentrations of fipronil in methanol solutions. Reproduced from ref. 290 with permission from The Royal Society of Chemistry. Copyright © 2018, The Royal Society of Chemistry. (b) Fluorescence images and spectrograms of **185** thin film test triethyl phosphate (solution and gas states). Parallel Reproduced from ref. 291 with permission from The Royal Society of Chemistry. Copyright © 2010, The Royal Society of Chemistry. (c) Schematic diagram, fluorescence spectrogram and linear range plot of the fluorescence detection system **186** for the detection of methyl paraoxon (MP). Society of Copyright © 2023, BioMed Central Ltd.

has begun to address pesticide residue testing, most of these applications are still at the scientific research level, and thus it necessary to extend these testing tools to agriculture as a top priority.

In addition, studies have shown that metal coordination polymers can detect heavy metals and trace chemicals that affect plant health. The carbazole-functionalized metal-organic polymer $[Cd_3(CBCD)_2(DMA)_4(H_2O)_2]$ -10DMA (Cd-CBCD, chemosensor 187) was developed as a highly efficient new fluorescent sensor for the detection of 2,6-dichloro-4-nitroaniline (DCN) by fluorescence quenching. 187 featured an LOD of 145 ppb together with a high quenching effect coefficient. 187 showed

R2=0.986

0 20 40 60 80 100 120 C_{MP} (µM)

0.2 0:0

biofunction for the removal or detection of chemicals in water systems, implying it can be used as a scavenger of environmental pollutants (Fig. 56a).²⁹³ In addition to carbazolefunctionalized metal-organic polymers for the identification of DCN, other metal coordination polymers can also detect DCN. For example, a new Ag(I) luminescent coordination

polymer, LCP1 (chemosensor 188), was developed with multisubstance recognition capability. It was found that 188 could specifically identify DCN, organosolvents and heavy metal ions by static quenching (Fig. 56b). The fluorescence quenching of 188 was ascribed to the FRET mechanism.²⁹⁴ In another example, a novel cadmium-based metal organic fluorescent

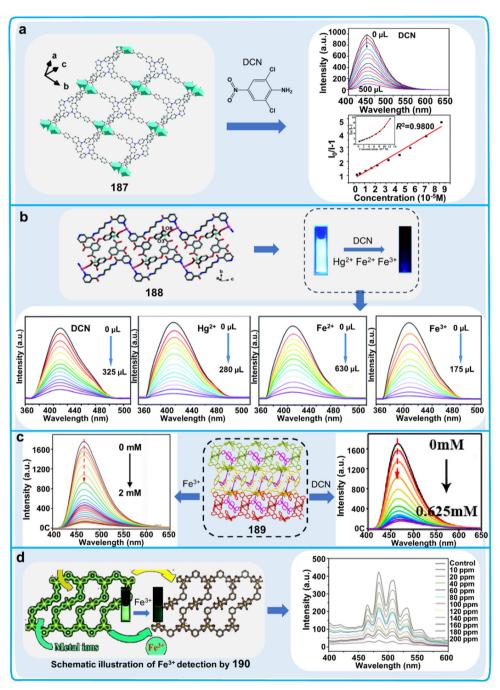


Fig. 56 Detection process and data graphs of organometallic fluorescent polymers for the detection of 2,6-dichloro-4-nitroaniline (DCN) or metal ions. (a) Fluorescence spectra and Stern-Volmer plots of different concentrations of DCN detected by 187. Reproduced from ref. 293 with permission from The Royal Society of Chemistry. 293 Copyright © 2019, The Royal Society of Chemistry. (b) Fluorescence images and titration spectra of 188 for the detection of different concentrations of DCN, Hg²⁺, Fe²⁺, and Fe^{3+, 294} Reproduced from ref. 294 with permission from The Royal Society of Chemistry. Copyright © 2020, The Royal Society of Chemistry. (c) Titration spectra of 189 detecting different concentrations of Fe³⁺ and DCN.²⁹⁵ Copyright © 2020, Elsevier. (d) Fluorescence images and titration spectra of different concentrations of Fe³⁺ detected by 190.²⁹⁶ Copyright © 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

polymer (chemosensor 189) was developed, which showed fluorescence turn-off behavior in water towards the pesticide DCN (Fig. 56c), with quenching efficiencies of up to 94.45%. ²⁹⁵ Interestingly, chemosensor 189 was also designed as an optical signal quenching fluorescent sensor for monitoring metal ions. Among fifteen metal cations, only Fe³⁺ could induce the quenching of the fluorescence emission signal of 189 in water (Fig. 56c). The fluorescence of Fe³⁺(a) 189 was recovered after the addition of ascorbic acid. This chemosensor showed an "onoff-on" mechanism for the recognition of DCN, Fe3+ and ascorbic acid, implying that the complex mechanism may reduce the detection accuracy of 189.295 The final example of metal ion recognition was a water-stable uranyl coordination polymer (chemosensor 190), which enabled the feasible and effective detection of Fe³⁺ in real river water samples (Fig. 56d). **190** was a 3D supramolecular framework that was formed by π – π and hydrogen bond interactions. This chemosensor has bifunctions for identifying and detecting Fe³⁺ and pesticides.²⁹⁶ If metal coordination polymers have dual detection function, that can be widely used to detect or remove pesticides and metal ions in water sources.

A well-known advantage of using organometallic polymers is their high sensitivity. However, their main disadvantage is that many metals and even heavy metals are toxic and can have a negative effect on plant health, and also there is radiation from radioactive metals. The raw materials for the preparation of organometallic polymers, the prepared organometallic polymers and the products after the use of organometallic polymers may all have a certain degree of toxicity.

Therefore, it is necessary to choose less toxic metals as the raw materials for the preparation of organometallic polymers, which is also a direction that needs to be the focus of research.

5.1.3 Molecularly/ion imprinted polymers. Molecularly imprinted polymers (MIPs) are polymers obtained by polymerization reactions between various functional monomers in the presence of a template molecule, which is covalently or noncovalently bonded to the polymer scaffold. When the template is removed after polymerization, a structure with sites designed to bind an analyte is produced, which is comparable to the template. Examples of constructing relevant molecularly imprinted polymers can be used to detect pesticides and plant toxins. Researchers constructed a novel microfluidic paper chip based on the FRET of nitrobenzoxadiazole (NBD) and CdTe QDs (chemosensor 191), which showed visual changes in ratiometric fluorescence for monitoring the concentration of 2,4-D (Fig. 57a). 191 showed a good concentration linear range of 0.56-0.80 µM with an LOD of 90 nM. This chemosensor was combined with cellulose paper for separating and detecting 2,4-D in bean sprouts and water samples. Further studies should focus on the integration of 191 with more sensitive sensors for the on-site and quantitative detection of pesticides.²⁹⁷ Another study established a molecularly imprinted membrane chromatography strip (chemosensor 192) combining electrostatic spinning, molecularly imprinted polymers, and fluorescent lateral flow test strips (LFTS) for the detection of pesticides. Then, based on the synthesis of a triazophos hapten-murine IgG/ fluorescein isothiocyanate conjugate (THBu-IgG-FITC) fluorescent

chemosensor with triazophos at the molecularly imprinted binding site on the membrane chromatography strip by competition to produce fluorescence changes as a method could realize the rapid detection of triazophos (Fig. 57b). This chemosensor showed a good linear concentration range of 20-500 µg mL⁻¹ with an LOD of 20 $\mu g \text{ mL}^{-1.298}$ In the case for the detection of plant toxins, researchers demonstrated a new sensor system for detecting aflatoxin B1 (AFB1 a common grain toxin), preparing molecularly imprinted polymer films (chemosensor 193) on the surface of glass slides to recognize aflatoxins and embedded spherical silver nanoparticles, which enhance the fluorescence signal of the analyte molecules, thereby increasing the QY and brightness (Fig. 57c). 299 193 showed a good performance for the measurement of AFB1 in samples of grain extracts that were naturally infected as well as samples that were spiked. This chemosensor realized molecular imprinting reactions that allowed the researchers to study the dissociation and binding of the toxin in real time. The last type of MIP combining a template and functional monomers detects metal cations by competition. For example, Alizarin Red S (ARS) and 4-vinylphenylboronic acid (VPBA) were chosen as the functional monomers and structural template, respectively, and precipitation polymerization was used to create ARS imprinted polymer particles (chemosensor 194). When Cu²⁺ and ARS formed a stable complex, it accomplished the purpose of detecting Cu²⁺ by separating ARS from 194 and causing fluorescence quenching (Fig. 57d), which was utilized for the detection of Cu²⁺ in water.300 The fluorescent sensors constructed by selecting the corresponding analytes as templates in the above-mentioned studies have high detection specificity. There are also studies in which the molecularly imprinted polymers have been used to prepare test paper/membrane chromatography strip-type sensors, which can be easily used for analyzing and detecting samples in the field.

By imprinting and polymerizing template ions in the imprinting process, ion-imprinted polymers are unique polymers that have the ability to selectively adsorb the template ions. In the following research examples, a batch of ionimprinted polymers for the selective detection of metal ions should be prepared based on various heavy metal ions as effective tool for the analysis and removal of contaminants in the living environment of plant. For instance, citric acid was used as a carbon source for the synthesis of CQDs via the hydrothermal method, and then an amidation procedure. The produced CQDs were attached as fluorescent groups on the surface of SBA-15 mesoporous molecular sieves. Then, the fluorescent sensor CQDs@Cu-IIP (chemosensor 195) was prepared via the surface blotting method, and Cu²⁺ could effectively quench the fluorescence of CQDs@Cu-IIP. Thus, CQDs@Cu-IIP was used as an ion-imprinted polymer for the detection of Cu²⁺ in river water (Fig. 58a).301 In addition to other IIPs for the detection of Cu2+, a type of quick and easy fluorescent ionimprinted sensor (FIIS) for Cu²⁺ detection was made by creating a fluorescent polymeric ligand. 4-(2-Aminomethyl)pyridinyl-Nallylnaphthalimide was employed as a fluorescent functional monomer, a layer of Cu(II) ion-imprinted polymer was coated on the surface of a PVDF membrane with a surface-functionalized

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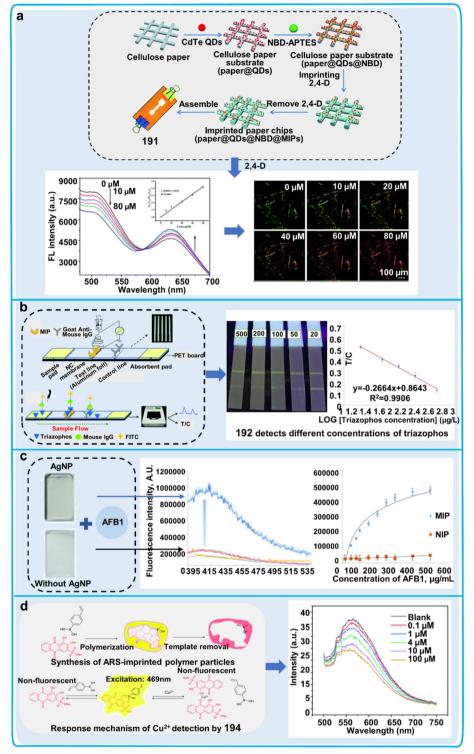


Fig. 57 Extraction mechanism and data tracing of molecularly imprinted polymers employed in pesticides, metal ions and toxin detection. (a) Procedure for fabricating 191 and its fluorescence spectra and images for the detection of 2,4-D. Reproduced from ref. 297 with permission from The Royal Society of Chemistry. 297 Copyright © 2020, The Royal Society of Chemistry. (b) Structure of test strips of 192, competitive fluorescence detection process for triazophos, images and calibration curves of test strips for the determination of distinct concentrations of triazophos.²⁹⁸ Reproduced from ref. 298 with permission from The Royal Society of Chemistry. Copyright © 2020, The Royal Society of Chemistry. (c) Fluorescence spectra of AFB1 detected by silverdoped and non-silver-doped 193. Reproduced from ref. 299 with permission from The Royal Society of Chemistry. 299 Copyright © 2022, The Royal Society of Chemistry. (d) Synthesis process of 194-imprinted polymer particles and their principle and fluorescence spectra for the detection of Cu^{2+,300} Reproduced from ref. 300 with permission from The Royal Society of Chemistry. Copyright © 2022, The Royal Society of Chemistry.

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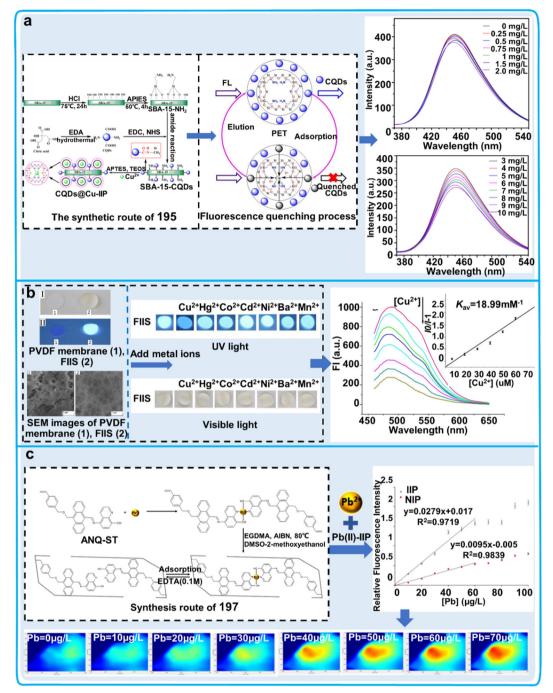


Fig. 58 Detection process and data graphs of ion imprinted polymers for the detection of metal ions. (a) Synthesis route of **195** and its quenching process and fluorescence spectrum for detecting $Cu^{2+}.^{301}$ Copyright © 2021, Multidisciplinary Digital Publishing Institute. (b) Images of **196** testing different metal ions under visible and UV light, and fluorescence spectra of 196 detecting $Cu^{2+}.^{302}$ Copyright © 2021, Elsevier. (c) Synthesis route of **197**, and its fluorescence curves and images for the detection of $Pb^{2+}.^{303}$ Copyright © 2020, Elsevier.

FIIS (chemosensor **196**). The fluorescence emission intensity of **196** decreased with an increase in the incorporation of copper(II) ions (Fig. 58b). The Cu²⁺ concentration in river water samples was effectively determined using **196**, which possessed a high degree of selectivity and sensitive recognition capacity for Cu²⁺. This study indicated that 1,8-naphthalimide can serve as versatile building block, implying that other fluorophores such as

coumarin and rhodamine can also have the same function. In another ion-imprinted polymer, anthracene-coupled styrene motifs and 5-amino-8-hydroxyquinoline served as significant chemical units in a precipitation copolymerization process to create a novel $Pb(\pi)$ -fluorescent IIP (chemosensor 197). 197 demonstrated a remarkably selective fluorescence switching property for Pb^{2+} and high fluorescence enhancement upon the

binding of Pb2+ (Fig. 58c), which proved its successful quantitative detection of Pb2+ in environmental water. Compared with normal fluorescent chemosensors, the imprinted polymer showed more selective properties for detecting ions in the environment.303 Ion imprinted polymers are similar to molecularly imprinted polymers, which they have high specificity for the analytes used as templates.

Overall, MIPs/IIPs have become popular as pesticide sensors due to their extremely high selectivity for target analytes and their durability in a variety of environments. However, they still have certain drawbacks, as follows: (i) the preparation of MIPs/ IIPs is still difficult and how to prepare these two types of imprinted polymers at lower cost and higher yields should be investigated. (ii) The specific recognition ability caused by the template may be lost after preparation and optimizing the preparation process of MIPs/IIPs will be an important condition to promote their application.

5.1.4 Other special fluorescent polymers. In addition to the above-mentioned three structural types of fluorescent polymers, combining fluorescent groups with proteins by means of hydrogen bonding to create supramolecular fluorescent polymers can effectively detect pesticide residues in agricultural products, soil, and water. In one example, FD@ALB (chemosensor 198), a new supramolecular sensor based on albumin (ALB) with a dualmode response to chlorpyrifos, was designed and prepared. 198 showed a good linear concentration range of 0-200 µM with an

LOD of 0.57 µM. It was combined with a smartphone, and then was used to perform the on-site detection of chlorpyrifos in a wide variety of environmental samples, including food, water, and soil samples, even at low concentrations (Fig. 59a). Another article reported the synthesis of a hydrazino-naphthalimidefunctionalized chitosan (NH-Chitosan) polymer (chemosensor 199), which was conducted through a chemical transformation process, 199 exhibited a turn-on fluorescence response by means of the particular chemical interaction between the incorporated hydrazino-naphthalimide functionalities and HCHO. Compared to small molecule chemosensors, the NH-chitosan random helical polymer chains in 199, which were derived from biopolymerized chitosan, had the ability to aggregate the marginally dilute concentration of HCHO surrounding the polymeric chains via minimal supramolecular affinities. The rapid chemical reaction between the hydrazino-naphthalimide groups and HCHO achieved an ultra-fast yellow fluorescent response to HCHO, and then realized the detection of HCHO in water (Fig. 59b). The development of new fluorescent polymers that do not belong to the traditional classification can sometimes get unexpected new detection modes, fast detection capabilities and high applicability.

In summary, the advantages of using these combinatorial systems include a variety of detection response modes and adaptability to a wide range of field environments. Therefore, there is great potential for the progression of novel combinatorial patterns and superior-performing fluorescent polymers.

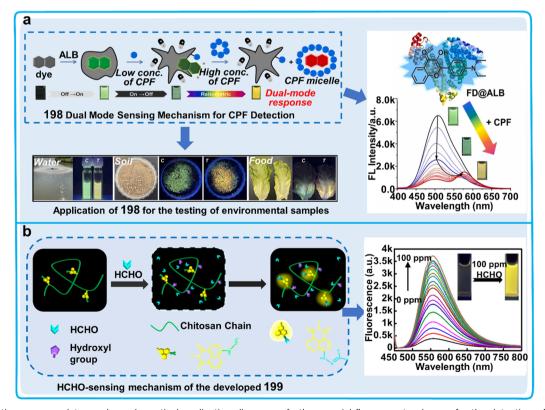


Fig. 59 Detection process, data graphs and practical application diagrams of other special fluorescent polymers for the detection of pesticides and toxins. (a) Dual-mode sensing mechanism of 198 for CPF and its titration spectrum for CPF and application to detect CPF in samples. 304 Copyright © 2023, Elsevier. (b) Sensing mechanism and titration spectra of HCHO by 199. 305 Copyright © 2018, the American Chemical Society.

5.2 Hydrogelator systems

The self-assembling network structures present in supramolecular hydrogels are developed by the non-covalent connections in hydrogelators.306 Supramolecular fluorogenic hydrogels generate fluorescence with an autonomic assembly procedure to generate potent nanoscale architectures for visualization. 307 In comparison to other types of chemosensor imaging, fluorescent supramolecular hydrogels have the advantages of versatility, biocompatibility, accessibility, low damage and high stability, and have been used in the fields of bioimaging and environmental monitoring (Table 12). 307,308 In the following section we introduce the applications of supramolecular fluorescent hydrogels in monitoring the living environment of plants, including detecting hazardous heavy metals in their surrounding environment and pesticide residues in fruits (Fig. 60).

There are some examples of the preparation of fluorescent supramolecular hydrogels that have been instrumental for assessing heavy metals in environmental water samples. A novel bifunctional AIE hydrogel (NDG, chemosensor 200) was established, which was ingeniously devised through a straightforward host-guest interaction. This involved a 1-naphthaleneacetic hydrazide amino-derivatized tripodal hydrazide, acting as the molecular host (NTS), and a tri-(pyridine-4-yl)-functionalized trimesoyl amide functioning as the guest (DTB) (Fig. 61a).309 Researchers delved into the cation-responsive attributes by incorporating and disseminating various metal ions in water into 200 and only the presence of Fe³⁺ caused the quenching of the fluorescence of this sensor. Moreover, with an increase in the Fe3+ dosage (0-0.45 equiv.), the emission intensity corresponding to the fluorescent response of 200 showed an impressive degree of linearity along the titration curve, and the fluorescence emission band decreased at 470 nm with an LOD of 5.33×10^{-9} M. Meanwhile, 200 exhibited bifunction for the removal and detection of metal ions and this chemosensor could be applied to selectively identify Fe³⁺ in real water samples. Another example involved the development of an expedient gelator (chemosensor 201), which was prepared using a phenylalanine derivative augmented with a quinoline ring harbouring a single N atom (3-phenyl-2-[(quinolin-2-ylmethyl)-amino]propionic acid, namely, 2-QF) (Fig. 61b).³¹⁰ The impact of diverse metallic ions on the photoluminescence of 201 was assessed, which revealed that the visible fluorescence response to Zn²⁺ of 201 was perceivable to the naked eye under UV radiation with a wavelength of 365 nm. Notably, the fluorescence intensity of 201 was substantially augmented by approximately 230-fold upon incorporating Zn²⁺, whereas the systems of 201-Cd or 201-Pb exhibited only a marginal increase in fluorescence intensity. These findings suggested that 201 exhibits potential as a superior sensor for the detection of Zn²⁺. 201 showed favorable membrane permeability, indicating that it can be applied for detecting metal ions in the environment and plants. Meanwhile, supramolecular fluorescent hydrogels have been used to detect heavy metal contaminants in plants. It was reported that fluorescent hydrogel-coated sensing gloves were created for monitoring the Hg2+ content in plants based on chemosensor 202 coated with a flexible paper/textile film (Fig. 61c).311

The applications of hydrogelator system-based fluorescent sensors for monitoring the health and environment of plants Table 12

	,	(1)	change 3	orescence 3		senching 3	
Limit of Target detection (LOD) analytes Applications	Detecting Fe ³⁺ in water via the form of fluorescence quenching	Detecting Zn^{2+} in water via the form of fluorescence enhancement	Detecting Hg ²⁺ in plants and water via the form of fluorescence color change		enhancement	Detected Lambda cyhalothrin in plants via the form of fluorescence quenching 3:	·
Target D) analytes	Fe ³⁺	Zn^{2+}	${ m Hg}^{2+}$	Dichlorvos		Lambda	aybolothrin
Limit of detection (LOI	5.33 nM	$0.145 \mu M$	8.00 nM	26.1 nM		$2.90 \ { m \mu g \ L^{-1}}$	
1) Solvents	$V_{\rm DMSO}:V_{\rm H_2O}=3.3:6.7$	Aqueous solutions	Aqueous solutions	Phosphate buffer solution 26.1 nM	(8 = Hd)	Aqueous solution	
$\lambda_{\rm ex}/\lambda_{\rm em}$ (nm) Solvents	300/470	317/377	365/501	360/465) 450/550	
chemosensor Name	NDG	2-QF	FHCP	GQDs/Enz/Gels		Cyclo-WW+Zn(II) 450/550	
Chemosen	200	201	202	203		204	

Ref. 309 311 311 312

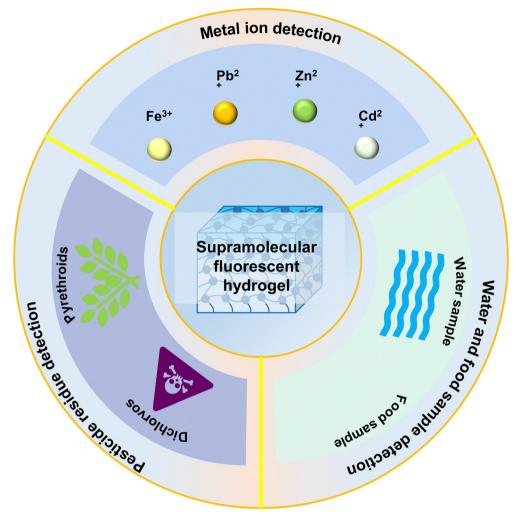


Fig. 60 Application of supramolecular fluorescent hydrogel in monitoring the living environment of plants and fruit safety. Supramolecular fluorescent hydrogel can be used to monitor plant health by detecting the heavy metals in the environment, pesticide residues in plants and pollution in water and fruit.

The results showed color changes from green to blue with an increase in the concentration of Hg²⁺. 202 showed remarkable analytical selectivity for Hg^{2+} with an LOD of 2.61×10^{-8} M. 202 was used to test Hg^{2+} in potherb and Canna leaf, and the measured results showed good consistency. Supramolecular hydrogels are not the only potential candidates for the evolution of a new class of digital apparatus, but also aid in the synthesis of smart supramolecular polymer sensors with superior fluorescent attributes. If widely used, supramolecular hydrogels can discover and help remove heavy metal ions in water samples and foods.

In addition to detecting heavy metals, researchers have developed supramolecular fluorescent hydrogels for detecting trace amounts of pesticides in agricultural products and the environment. It was reported that researchers synthesized new fluorescent hybrid materials comprised of enzymatic entities affixed to an L-phenylalanine-derived bis(urea) supramolecular hydrogel platform coupled with graphene quantum dots (GQDs/ Enz/Gels, chemosensor 203) for the qualitative analysis of organophosphates (Fig. 62a).312 AChE induces the degradation

of acetylcholine (ACh), yielding choline. Subsequently, choline is incessantly oxidized by choline oxidase (ChOx), leading to the production of H₂O₂ and culminating in photochemical suppression of the integrated gel assemblies. Upon exposure to UV radiation at 365 nm, a substantial enhancement in visible fluorescence image intensity was observed for 203 impregnated with dichlorvos as the analyte concentration increased from 1 \times 10^{-6} to 1×10^{-3} M. The anti-cholinergic potency of dichlorvos against AChE demonstrated a linear response in the range of 1.25×10^{-8} to 1.25×10^{-4} M, indicating that the low molecular weight hybrid hydrogels can also have high sensitivity and stability for detecting pesticides. Considering that AChE and ChOx can be combined in 203 as a signaling unit, this chemosensor can be developed as an enzymatic activity detection kit. Another visual platform (chemosensor 204) was constructed using a cyclo-ditryptophan (cyclo-WW) + Zn(II)-based photoluminescent hydrogel, which showed good ability to detect lambda cyhalothrin (LC) (Fig. 62b).313 In the process of oxidative PET, post formation of a coordination complex between the surface group of 204 and LC, this complex triggered non-

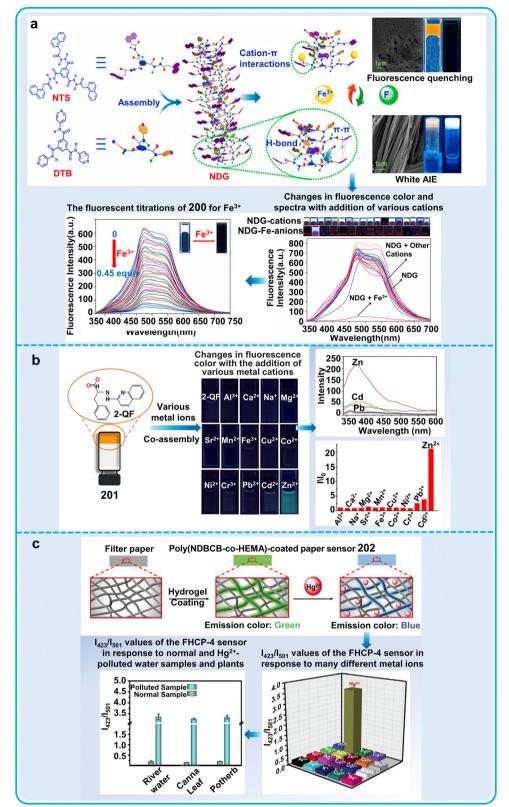


Fig. 61 Detection process, data graphs and practical application diagrams of supramolecular fluorescent hydrogels system for detecting ions in plant surroundings. (a) Construction of 200 and the possible mechanisms, as well as the fluorescence effect and data statistics about the sensing of Fe^{3+} and other cations. Opyright © 2020, Elsevier. (b) Chemical structure of 201 and the fluorescence effect and data statistics of Zn^{2+} and other metal ions. Copyright © 2020, Elsevier. (c) Preparation of the fluorescent hydrogel-coated paper (FHCP, 202) for Fe^{2+} detection in water and food samples. Copyright © 2020, WILEY-VCH Verlag GmbH.

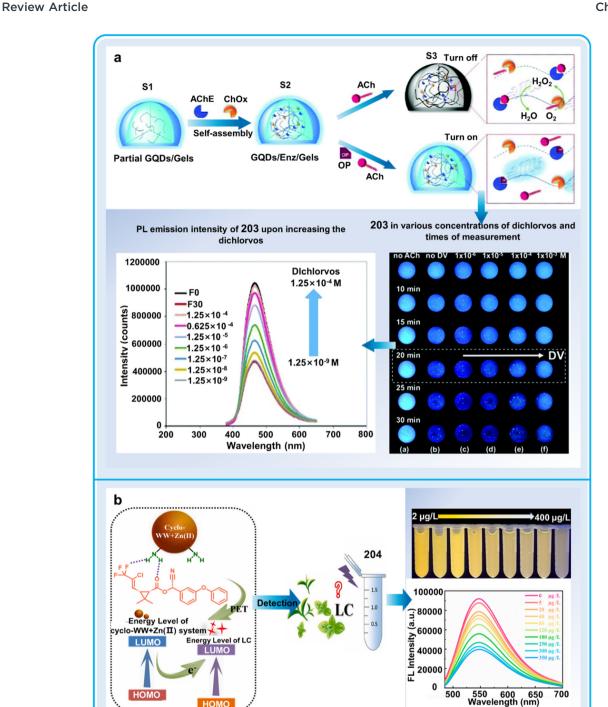


Fig. 62 Detection process, data graphs and practical application diagrams of supramolecular fluorescent hydrogel system for the detection of pesticides in the living environment of plants. (a) Proposed mechanism of hybrid 203 for organophosphate pesticide detection and the fluorescence effect and data statistics after adding dichlorvos. 312 Reproduced from ref. 312 with permission from The Royal Society of Chemistry. Copyright © 2021, The Royal Society of Chemistry. (b) Schematic illustration of the sensing mechanism and the fluorescence effect of 204 and data statistics after adding lambda cyhalothrin. 313 Copyright © 2022, Elsevier.

radiative emission upon relaxation from the excited electronic state into the ground state. Under these conditions, 204 acted as an electron donor, providing electrons to the electron acceptor LC. When subjected to LC, the intensity of the yellow luminescence emitted by 204 progressively diminished with an increase in the concentration of LC. 204 exhibited outstanding precision and

robust stability when assessing pesticides in actual samples, which can provide guidance for developing polypeptide-based biosensors. The above-mentioned studies developed a miniature hybrid hydrogel confined to a glass slide, or developed a smartphone-assisted sample-to-answer analyzer, which can be used as a rapid, convenient, and high-throughput sensor for the detection of pesticides.

In conclusion, the environmental friendliness and high sensitivity of supramolecular fluorescent hydrogels make these chemosensors suitable for detecting heavy metals in the environment and pesticide residues in plants and food. However, there are also some challenges that need to be considered, as follows: (i) modification of the backbone structure frequently perturbs the stability of the hydrogel networks and (ii) the leakage of fluorescent materials combined with the accumulation of chromophores may induce a reduction in optimum emission intensity and potential quenching of fluorescence. Therefore, improving the stability of supramolecular fluorescent hydrogels will be an important aspect to promote their practical application.

6. Analysis of fluorescent chemosensor data

6.1 Techniques for fluorescent chemosensor data analysis

The processes for dealing with the data obtained from fluorescent chemosensors mainly involve two steps, image capture and image processing. High-quality and resolution fluorescence images can maintain the integrity, accuracy and repeatability of the results from microscopy. High precision analytical techniques and statistically rigorous quantification methods are frequently required to gain enhanced comprehension of the intricate biological mechanisms for governing plant health and monitoring the living environment of plants. In the following section, we describe these two steps in detail.

For image capture, fluorescence microscopy, including fluorescence microscopy, confocal laser scanning microscopy (CLSM), two-photon fluorescence microscopy, fluorescence lifetime imaging microscopy (FLIM), stimulated emission depletion (STED), single molecule localization microscopy (SMLM), structured illumination microscopy (SIM), and total internal reflection fluorescent microscope (TIRFM) are frequently used (Fig. 63a). (1) Fluorescence microscopy can only visualize presliced specimens and does not have the potential of optical slicing. In the case of three-dimensional samples thicker than 2 μm, the whole sample fluoresces, causing defocused emissions, obscuring the focal plane detail and reducing the image contrast. However, it also has some advantages such as the utilization of a mercury are lamp or xenon lamp to offer a comprehensive spectral range spanning the UV, visible and NIR bands. 314 (2) CLSM represents an alternative technique for recovering thin fluorescent sections through optical isolation of fluorescence emission within the imaged plane, facilitating the visualization of plant cells in thick sections at high resolution. However, despite point-scan imaging, the imaging speed of CLSM is slow due to the limited laser excitation, narrow frequency band, and high intensity laser radiation.³¹⁵ (3) Two-photon fluorescence microscopy allows non-destructive examination of biological

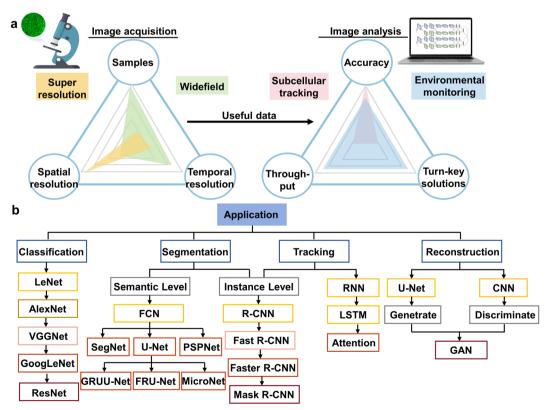


Fig. 63 Potential methods for the analysis of fluorescent chemosensor data from monitoring the health and living environment of plants. (a) Image acquisition and analysis approaches for the above-mentioned areas. (b) Various networks are constructed according to the specific processes in image analysis. © 2021, Elsevier Ltd

specimens in three-dimensions with submicron precision. Excitation of two-photon fluorophores originates from dual photon

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absorption simultaneously. This distinctive emission mechanism possesses several advantages such as diminished sample photodegradation, reduced photoblinking, improved penetrative depth, and producing superior contrasting images.³¹⁶ (4) FLIM, a microscopy strategy dependent on the nanosecond fluorescence lifetime of molecules, has gained immense popularity due to its superior sensitivity to the environment and variations in the structure of molecules. This technology shows advantageous characteristics such as identifying spectrally overlapping fluorophores by the fluorescence lifetime, detecting fluctuations within fluorophore molecular environments, measuring quenching dynamics, and executing self-referenced assessment. However, FLIM analysis needs technical proficiency and has high computational costs, extensive photon usage for fluorescence lifetime determination, and susceptibility to multiple factors ranging from molecular interactions/binding activities to environmental conditions (temperature, viscosity and pH).317 (5) In the case of SIM, a collection of complex patterns of intensity is utilized to illuminate the targeted object, thereby facilitating the reconstruction of an accurate image of the subject material. Its advantages include straightforward sample processing, swift imaging rate, expansive imaging field, and widespread adoption in biology. However, SIM displays low tissue penetration depth, restricting its application in single-cell imaging due to the substantial scattering caused by its low excitation power density.³¹⁸ (6) SMLM is an imaging technique capable of overcoming the diffraction obstacle to yield super-resolution images. The random switching between on and off states is followed by the collection of substantial photons to computationally simulate and merge the locations of all individually activated fluorophores to generate a superresolution image. However, this technology is associated with some challenges such as complex sample processing procedures, fluorophore photobleaching, and substantial computational requirements.319 (7) STED is a novel enhancement of confocal microscopy, which is regarded as the primary far-field super-resolution imaging technology applicable to cell observation. Its proficiency in cell imaging and three-dimensional chromatographic capacity have attracted considerable attention in biological research. Nevertheless, these advantages are counterbalanced considering its potential cellular phototoxicity, photobleaching, and advanced technical proficiency.³²⁰ (8) TIRFM is complex optical technology, enabling the activation of fluorophores within an exceptionally thin axial zone, and then producing a satisfactory S/N ratio. By exploiting the inherent characteristics of an evanescent wave or field confined to a specific specimen vicinity immediately adjacent to the interface between two media possessing different refractive indices, it facilitates the comprehensive observation of the entire wide field rather than utilizing point-by-point scanning. The fundamental limitation of TIRFM as an innovative detection tool in biochemical and chemical research is its inability to utilize selective fluorescent chemosensors specifically.³²¹ In short, each of the above-mentioned eight primary techniques has

advantages and limitations, indicating that we should select the optimal equipment depending on the sample under investigation and the associated scientific requirements.

The traditional methodologies for processing microscopic images mainly include morphological differentiation, image fusion, edge detection, classification, region growing, and feature extraction. These techniques typically necessitate the expertise of computational experts, who are scarce within plant science and necessitate complex computational processes. Additionally, traditional fluorescence microscopy images consistently exhibit relatively diminished resolution and inferior S/N ratio owing to the restraints imposed by imaging systems and the restrictions of diffraction. Consequently, conventional image processing methodologies are often insufficient for efficient data interpretation.322 Deep learning (DL), a novel approach representing data learning, is a significant segment of artificial intelligence (Fig. 63b). 323 For microscopic image analysis, scientists are progressively incorporating DL into various complex challenges such as cellular components, subcellular structures, tissue architectures, and the diversity of environment. Specially, DL in images processing involves four main steps including image classification, image segmentation, target tracking and super-resolution reconstruction.324 (1) Classification. Establishing classification tools capable of distinguishing diverse pollutants within the living environment of plants, specific cell stages or subcellular structures can provide important insights into plant health. This may enable farmers or chemical engineers to adopt effective strategies for managing plant health. Presently, convolution neural network (CNN), including ResNet, AlexNet, and LeNet, are prevalent in classification procedures. Typically, initial DL-based classification exhibits higher accuracy and greater efficiency compared to its conventional counterparts. (2) Segmentation. Establishing boundaries around regions of interest is an indispensable phase in microscopic image analysis, facilitating focus on data-rich areas of significance. Intracellular compartment segmentation supplies quantifiable data regarding cell structure and functionality. Dl-Based segmentation methodologies are categorized into two types, instance-level segmentation and semanticlevel segmentation, depending on the incorporation of a fully interconnected layer. Prioritized semantic-level and instance-level segmentation algorithms originate from the U-Net and R-CNN models, respectively. (3) Tracking. Assessing the viscosity of cells, infection of pathogens or distribution of pollutants within the living environment of plants is fundamental for discerning significant plant health signals. The networks employed for localization predominantly utilize the methodologies of recurrent neural networks (RNNs). With advancements in long short-term memory (LSTM), issues related to gradient explosions and gradient vanishing have been effectively managed. Consequently, data such as the prevalence of environmental pollutants, early plant health diagnosis, or the interaction between plant-environment interactions can be more accurately recorded. (4) Reconstruction. Image reconstruction involves generating a two-dimensional or threedimensional visualization from fragmented or incomplete data. The discipline of microscopy image interpretation includes techniques such as super-resolution reconstruction, denoising, and three-dimensional reconstruction to generate high-quality and

comprehensive images. DL-based image restoration techniques can facilitate the rapid capture of photosensitive specimens and promote high-quality and long-term dynamic observation of plants. Methods integrating GANs have been employed to facilitate super-resolution imaging across various microscope platforms, enabling the conversion of diffraction-limiting signals into super-resolution images. Furthermore, recent developments in augmented intelligent microscopy and proficiency in deep learning technologies are beneficial for managing plant-environment interactions in sustainable agriculture.

6.2 Networking of fluorescent chemosensor data

The spatial and temporal complexity of the health and surrounding ecosystems of plants pose substantial challenges to accurately enforce plant health management. Despite the extensive reliance on remote sensing techniques or sophisticated mass spectrometry chromatography tandem methods, they are limited by the spatial and temporal resolution, labor intensive and resource consuming. As illustrated in Fig. 64, fluorescent chemosensors can be effectively employed to monitor the soil environment, the quality of irrigation water and plant health in a timely manner and accurately. Firstly, fluorescent chemosensors can detect moisture, pesticides, nutrients, heavy metals, microorganism diversity and ions to evaluate the soil environment. Soil functioning as a living ecosystem can offer various services such as food and fibrous yield, water quality and supply, managing pest and disease, modulating the atmospheric composition, climate regulation and biodiversity conservation. Wholesome soil produces robust plants, significantly contributing to plant proliferation and maturity. Any pollution of the soil with detrimental substances such as inorganic pollutants and organic toxins can disrupt plant assimilation

and metabolic activities, resulting in impaired plant growth and developmental disorders. Meanwhile, soil organic matter functions as an indispensable nutrient source for plants, providing crucial materials for maintaining soil texture, regulating pH, and storing nutrients. Insufficient soil organic matter can hinder plant growth and potentially lead to nutritional deficiencies. Secondly, fluorescent chemosensors facilitate the continuous monitoring of irrigation water such as heavy metals, pesticides, and ions, which have a direct impact on plant growth. Irrigation is crucial in addressing food insecurity and water scarcity issues. High-quality irrigation water can provide sufficient water together with nutrients that can promote plant physiological metabolism, facilitate robust root systems evolution, and enhance crop vitality. In contrast, low-quality irrigation water can decrease plant nutrient assimilation capabilities, facilitating the transfer of damaging pathogens and pests, thereby increasing plant disease incidence. For example, heavy metals in irrigation water are found to be assimilated by plants, and subsequently accumulated across multiple plant tissues, which not only influence plant root growth and above-ground biomass production but also pose potential health risks to humans. Thirdly, fluorescent chemosensors offer an invaluable tool to evaluate plant health by evaluating the nutrient uptake dynamics, signaling molecule synthesis, cell components, metabolites, and food quality. For example, hormones serve as critical signaling molecules and are essential for governing numerous plant physiological processes, such as growth, metabolism, organogenesis, reproduction and stress resistance, which significantly affect plant growth and survival. A comprehensive array of metabolically diverse molecules with diverging structural and functional attributes, serving a myriad of roles in plant health, by modulating plant resilience amidst persistently

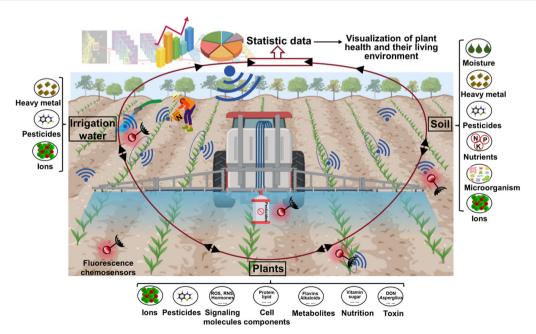


Fig. 64 Fluorescent chemosensor networks for monitoring the health and living environment of plants. Fluorescent chemosensors can monitor the health status and living environment of plants. Then the collected data will be analyzed and provide accurate suggestions for plant health regulation.

Chem Soc Rev

fluctuating environmental variables together with both non-living stressors and biological aggressions. Therefore, the use of fluorescent chemosensors provides real-time data and a feasible solution to improve our capability to manage plant health.

7. Conclusions and outlook

This work provides a comparatively comprehensive summary and analysis of studies during the last decade towards the design of fluorescence chemosensors including small-molecule, nano- and supramolecular-chemosensors in regulating plant health. Chemosensors can provide a better understanding of the plant health status under abiotic and biotic stresses, and different nutrient utilization, as well as their living environments. We described the structural features of these chemosensors, their fluorescence characteristics, response mechanism and the intrinsic multifunction. This fluorescent technique will contribute to the enhanced comprehension of the complex interdependence among the environment, human behavior and plant health.

When initiating the detailed design processes for a state-ofthe-art fluorescent chemosensor to monitor the health and surroundings of plants, it is vital to establish a connection between the fluorescence features of chemosensors and the requirements of plant health regulation. Therefore, future studies should focus on the following aspects: (1) increased emphasis must be placed on developing two-photon and NIR-II fluorescent probes. It is universally acknowledged plant imaging presents difficulties distinct from other model systems because of its robust endogenous auto-fluorescence attributed to chlorophyll in the wavelength range of 400-800 nm. The NIR laser utilized by two-photon and NIR-II fluorescent chemosensors could not only avoid the autofluorescence within plant tissues, but also achieve superior imaging resolution compared to traditional fluorophores. (2) To enhance comprehension of the distribution, translocation and metabolism of signaling molecules under biotic or abiotic stresses, fluorescent chemosensors should be endowed with sub-organelle targeting potential including mitochondria and plasma membrane.

By pinpointing their location at the subcellular level, the elucidation of signaling molecules involved in plant health can be enhanced. (3) Fluorescent nano-chemosensors constructed from QD, COF and MOF materials have made great progress in detecting agricultural pollutants with good recyclability. Future endeavors should concentrate on minimizing the nano dimensions of the aforementioned materials for improving the functionality within plant tissues such as molecular imaging, pesticide release, and labeling signaling molecules. (4) Presently, existing detection methods for plant health are primarily concentrated on individual plant tissues, and thus implementing comprehensive field testing utilizing portable smart devices poses a novel hurdle in future investigations. (5) Further studies should devise super-resolved fluorescent chemosensors to determine the subcellular distribution and transportation mechanism of HPPD in plants to monitor the plant health condition under abiotic stress. Meanwhile, it will serve

as an useful tool for in vivo and in vitro inhibitor screening. The inhibitors can compete with the binding sites of proteins with fluorescent chemosensors. When the binding affinity of inhibitors with proteins surpasses their affinity towards fluorescent chemosensors, they may be regarded as highly effective inhibitors. (6) AI should be applied in processing fluorescence images by improving image quality, extracting relevant information and analyzing data. Compared with the vision of professionals, AI technologies have some advantages such as improving image quality with reducing noise, correcting illumination, enhancing contrast, precise analysis by segmentation images, identification of interesting objects, tracking dynamics of biological processes by analyzing temporal changes in images, and comprehensive data analysis by integrating fluorescence images data with other types of data including genomic or proteomic data.

Conflicts of interest

There are no conflicts to declare.

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