

## Review

# Advanced electrochemiluminescent approaches for contaminant detection in food matrices using metal-organic framework composites

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## ABSTRACT

Metal-organic frameworks (MOFs) are highly valued for their electronic and optical capabilities in food sample analysis. Implementing MOF-based sensors is crucial for public health safety. This review centers on electrochemiluminescence (ECL) MOFs for monitoring food samples, highlighting signal changes from combining MOFs with  $\text{Ru}(\text{bpy})_3^{3+}$ , TPrA, nanomaterials, and biomolecules. It systematically reviews the development, mechanisms, signal pathways, and findings related to ECL MOF food sensors. Notably, immobilizing ZIF-8 and various metals with transducers like gold nanoparticles enhances ECL signals, enabling effective monitoring across media types. Moreover, MOFs excel in co-reactant processes, resonance energy transfer, and catalytic redox reactions for detecting analytes in food, presenting opportunities for advanced sensory analysis and the creation of cost-effective, sensitive signal transducers for food safety and quality control.

## 1. Introduction

Metal-organic frameworks (MOFs) are materials with highly customizable porosity and well-defined structures, making them versatile for a wide range of applications. Due to their unique properties, MOFs are used in various fields, such as energy storage, environmental remediation, food packaging, drug delivery, and medical diagnostics (Abánades Lázaro et al., 2024; Baumann et al., 2019; Mohan et al., 2024). Their tunable pore sizes and high surface areas are ideal candidates for gas storage, catalysis, and separation technologies. Furthermore, their structural diversity allows for the design of MOFs specifically tailored for different applications, demonstrating great potential in addressing various societal and industrial challenges (Duan et al., 2024; Mohan et al., 2022; Perl et al., 2023; Shi & Zhao, 2024; Xue et al., 2022). The coordination of the metal center and ligands resulted in stable MOF crystalline structures that can be easily fabricated using both inorganic and organic materials (Connolly et al., 2019). With their organized building blocks, MOFs have been used to address societal issues such as food and water quality analysis. The growing population and demand

have led to contamination of food sources due to human activities, industrial processes, and climate change. It is crucial to find a solution to ensure food quality at the grassroots level for food contaminants detection, including regular chemicals, metal ions, and organic and inorganic substances with different electronic properties (Hou et al., 2023; Liang et al., 2023; Onyeaka et al., 2024; Saidon et al., 2024).

The development of electrochemiluminescence (ECL) techniques for monitoring contaminants has been driven by the desire to ensure food quality (Niu et al., 2024; Yang, Wang, Zhang, et al., 2024). Electro-generated ECL is photon emission from a luminophore due to an electron transfer process triggered by an electrochemical reaction. ECL began in the 1920s and evolved in the 1960s with works by Professor Allen J. Bard (Geske & Bard, 1959). It quickly became a powerful electroanalytical technique with the development of the sensor. Molecular electrochemistry is crucial for understanding ECL generation mechanisms and studying new luminophores (Fiorani et al., 2018; Zhen et al., 2024). Furthermore, ECL materials sensors have various applications across various industries, including medical diagnostics, environmental monitoring, and food safety (Yang, Tian, Song, et al., 2024; Yang, Zheng,

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Wang, et al., 2024). These sensors can detect small amounts of substances with great accuracy and precision, making them an excellent choice for sensitive detection.

The consumption of low-quality food that lacks essential nutrients has been linked to the development of serious chronic diseases such as heart disease, diabetes, and obesity. Therefore, researchers must prioritize the thorough analysis of the food consumed and implement effective monitoring techniques to ensure its quality and nutritional value (van Dijk et al., 2021; Wang, Dou, et al., 2023). Food contaminants, including chemicals and biological and physical substances, can enter the food supply chain through various pathways from the farm to the table (Suzuki et al., 2020). Many different forms of contamination pose a threat to the safety of our food supply. These include bacteria, heavy metal ions, pesticides, and insecticides. When these contaminants enter the food supply chain, they can cause a range of illnesses and infections in the body, posing a severe risk to public health (Kebede et al., 2024; Wang, Walker, et al., 2020).

The global food industry has over 350,000 registered chemicals and mixtures. These food additives make their way into the food chain through various food products. Regulatory bodies like the European Food Safety Authority and the Food and Drug Administration (FDA) in the U.S. must approve food additive ingredients. However, there are currently no specific labeling regulations for food additive concentration. Generally, low concentrations are considered safe (Dinu et al., 2020; Tralau et al., 2021). In addition, soil quality is a significant factor for agriculture-based foods, in addition to food additives. Approximately 13 % or more of the grain grown in acidic soils causes food toxicity, which can affect human health. Soil can also negatively impact and imbalance metal oxides and hydroxides through interactions with other substances, leading to low bioavailability (Lei, Cheng, et al., 2024; Li, Chen, et al., 2023).

Recently, a promising focus has been on developing materials to analyze contaminants in food samples. Various techniques like electrochemical, spectroscopic, phase extraction, and spectrometric methods have been used with specially designed metal, carbon, and silica-based porous materials, nanomaterials, carbon materials, covalent, hydrogen, and coordination metal organic frameworks have emerged as promising candidates for contaminant analysis (Huo et al., 2024; Li, Cai, et al., 2024; Li, Jin, et al., 2024; Lu, Luo, et al., 2024; Mirzaei Karazan et al., 2024; Salamat & Soyulak, 2024). A critical report has highlighted the use of the ECL sensors system, which combines a triple helix structure with CRISPR/Cas12a to detect trace pesticides using ZIF-8. This approach uses an aptamer with auxiliary sequences to form a target converter, exposing the aptamer for binding. Upon binding, rolling circle amplification (RCA) was initiated. The RCA product was then encoded with a DNzyme/substrate unit, activating the CRISPR/Cas12a system and serving as quenching probes for signal output. This method shows strong selectivity and sensitivity in detecting acetamiprid (Li, Chen, et al., 2024). In an example, 3, 4, 9, 10-perylene-tetracarboxylic acid (PTCA) was selected as the luminophore, and a terbium metal-organic gel (MOG) was prepared to act as a co-reaction accelerator. The MOG provided a large surface area for PTCA immobilization, which catalyzed the reaction with potassium persulfate ( $K_2S_2O_8$ ) to generate sulfate radical anions. This process accelerated the electron transfer rate, improving ECL efficiency. However, due to the specific binding effect between the patulin aptamer and patulin, the ECL signal was quenched in patulin presence. This relationship allowed for measuring a wide range of PAT concentrations (Xiang et al., 2023). ECL sensors are recognized for their high electron transfer capabilities when interacting with analytes. In a biocathode-reducing oxygen system, electron transfer originates from *E. coli* O157:H7 bacteria due to their electrochemical activity. Microbial fuel cells facilitate the reduction of oxygen in an ECL system, allowing for the monitoring of *E. coli* O157:H7 levels in food (Chen, Tao, et al., 2023). The ECL sensing system has proven to be more efficient than other techniques, such as fluorescence and spectrometry in various analytical applications. This enhanced efficiency can be

attributed to its unique mechanism, which allows for high sensitivity and specificity in detecting analytes. By integrating MOFs with the ECL system, researchers have the potential to develop highly sensitive analytical tools specifically designed for food sample analysis due to tuned properties providing better interaction with the target molecules.

In recent years, researchers have shown particular interest in MOF materials with significant potential across various sectors of the food industry, including food packaging, sensing, flavor additives, and more (Cheng et al., 2021; Leelasree et al., 2020; Sharanyakanth & Radhakrishnan, 2020; Zhang, Lou, et al., 2021). The particular focus on MOF sensors for food, environment, and clinical samples has been explored based on spectroscopic and electrochemical activities (Kathuria et al., 2023). In addition, nanomaterials and carbon-based materials such as electrochemical, luminescence, and ECL sensors have been studied with insights into sensing mechanisms, selection of the analytical parameters, and stabilities (Abedi-Firoozjah et al., 2024; Lu, Zhang, et al., 2024). Vidic et al. provided essential insights on ECL sensing for water pollutants and industrial chemicals, including organic compounds, pharmaceuticals, and cyanotoxins (Sentic et al., 2023). Our previous review discussed luminescent and electrochemical monitoring of food contaminants (Mohan et al., 2023). It has been observed that review studies on ECL MOF food sample analysis have gained limited attention, while microfluidic ECL approaches and ECL reactions in solutions and on the surface of microbeads have been discussed (Kirschbaum & Baemner, 2015; Wang & Su, 2021). This review focuses on the current demand for food sample analysis using MOF ECL sensors, one of the unrevealed areas with new findings and challenges that will open a gate for researchers. It will inspire the development of reusable and stable MOF food sample monitoring tools with high sensitivity under moisture, hydrothermal, and pH conditions, potentially revolutionizing the food industry. The review highlights a set of excellent works that have been developed to create MOF ECL sensors for analyzing food samples with precision. It offers a detailed comparison of metal and carbon materials with MOF ECL sensors, focusing on the material science aspect of food sample analysis. Moreover, this research addresses the urgent need for cost-effective, rapid, and highly responsive devices for monitoring contaminants in the complex matrices found in food products. The findings of this investigation have significant potential value for academic and industrial purposes in enhancing the quality of analytical tools used in food testing protocols.

## 2. ECL food samples analysis system

The food analysis process starts with lab samples and moves to real sample analysis applications using suitable techniques and materials. Real sample analysis is necessary to determine analyte concentration in food samples (Ghasemi et al., 2024). It follows sample collection, grinding, and enzymatic and non-enzymatic hydrolysis to obtain an extract used for sensing. Hydrolysis has the advantage of stability and intends to mimic the biochemical and physical processes in the human digestive system compared to strong acid and high-temperature microwave digestion (Fig. 1) (Jain et al., 2024; Santana et al., 2024).

ECL food sensors have been designed with various porous, metal, and carbon-based materials for tuned electronic and multifunctional sites suitable to interact with analytes. This is for designing real-time analysis of food samples (Fig. 2). ECL food sensors function by applying electrical potential to electrodes within an electrochemical cell. This cell contains luminescent species, including polycyclic aromatic hydrocarbons, metal complexes, quantum dots, and nanoparticles. These luminescent species interact with the applied potential to facilitate the detection and analysis of various components within food samples, providing valuable insights into food quality and safety (Kuang, Li, Ji, et al., 2024). ECL sensors with donor materials can choose the quenching effect in resonance energy transfer system (RET) and sensitivity (Li, Cui, et al., 2021). The typical donor materials are metal-based nanoparticles and carbon-based modified composite nanomaterials. Combining these

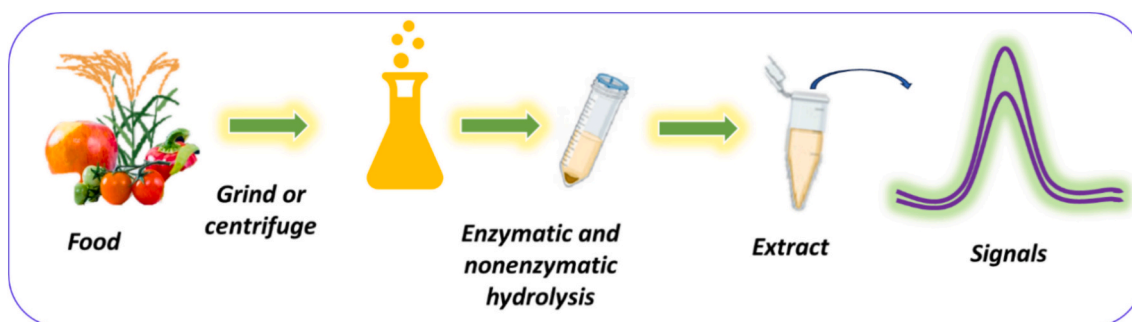


Fig. 1. Schematic representation of sample preparation procedure and analysis.

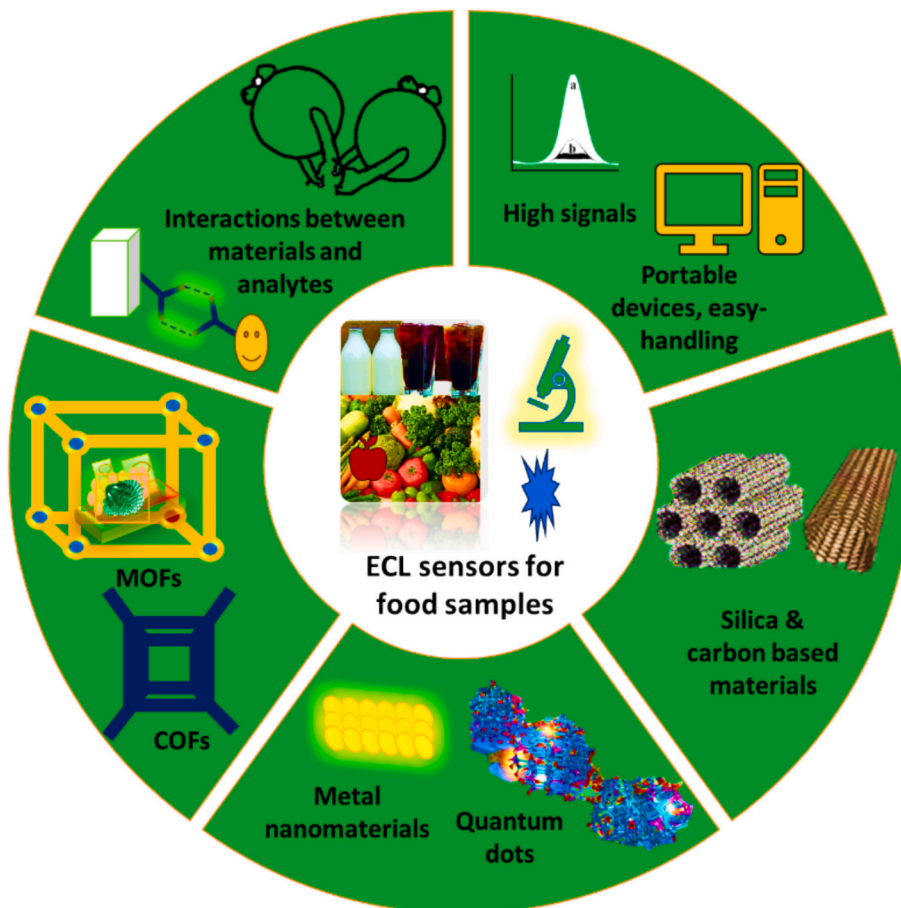


Fig. 2. A schematic representation of materials used for ECL sensing of food samples.

nanomaterials with MOFs makes the susceptible materials suitable for the ECL platform. Graphene oxide (GO) and silver and gold nanomaterials can also be used as composite materials to enhance specific surface areas and compatibility. The immobilization can help in spectral overlapping in the ECL-RET process between labeling materials (Fan et al., 2023; Li, Ma, et al., 2021).

It is a challenging task that requires sensitivity and selectivity, as well as expensive instruments and specific handling procedures for monitoring food samples and analyzing their safety. To develop affordable and fast analysis devices, researchers must address certain limitations, such as sensitivity, speed, selectivity, and handling (Xie et al., 2024). It is essential to explore various ECL sensing platforms to understand the ECL sensing system comprehensively. These platforms are developed using different materials, including conductive polymers, metal nanoparticles, and biomolecules, such as proteins and nucleic

acids. Additionally, incorporating enzymes can enhance sensitivity and specificity, making the sensors more effective in detecting target analytes. Nanomaterials also play a crucial role by providing larger surface areas and improving the overall performance of the sensors. By examining these components in detail, researchers can better appreciate the intricacies and capabilities of ECL sensing systems.

### 2.1. Tris(bipyridine)ruthenium(II) ( $\text{Ru}(\text{bpy})_3^{2+}$ )-based ECL system

Tris(bipyridine)ruthenium(II) ( $\text{Ru}(\text{bpy})_3^{2+}$ )-based ECL system utilizes ruthenium complex  $\text{Ru}(\text{bpy})_3^{2+}$  as the luminophore, which undergoes redox reactions to emit light. This system is widely used in bioanalytical applications due to its high sensitivity and selectivity. The loading of  $\text{Ru}(\text{bpy})_3^{2+}$  with metallic materials enables the rapid activation of the sensing platform while ensuring reproducibility (Li, Jin, et al., 2024).

Researchers are showing interest in using materials-based ECL sensing to analyze food samples. New sensors using co-reaction promoters Ru(bpy)<sub>3</sub><sup>2+</sup>/tri-n-propylamine system to enhance ECL signals with CdSe@ZnSe and CNTs have been used as ECL sensors to detect low levels of melamine in milk samples with limit of detection (LOD) of  $3.3 \times 10^{-12}$  M (Q. Wu et al., 2024).

A recent report demonstrated the strong anodic ECL emission of Ru(bpy)<sub>3</sub><sup>2+</sup> at an electrode modified with an ionic liquid, specifically N-butyl pyridinium tetrafluoroborate, without requiring any additional co-reactant. Notably, methylene blue (MB) effectively absorbs energy from the ECL of Ru(bpy)<sub>3</sub><sup>2+</sup>, establishing a robust ECL RET system. This interaction significantly reduces the ECL signal, which is pivotal for accurate glucose detection (Wang, Jia, et al., 2024). In another example, Yang et al. utilized a system comprising Ni-MOF@Ru(bpy)<sub>3</sub><sup>2+</sup> and Au NPs@TiO<sub>2</sub>, where Tripropyl Amine (TPA) served as the luminescent signal. In this setup, Ni-MOF acted as a carrier for the luminescent reagent, while gold nanoparticles facilitated electron transport. Additionally, TiO<sub>2</sub> enhanced luminescence through its interaction with Au NPs, enabling the detection of permethrin in vegetable samples with an ultra-trace detection limit of  $3.3 \times 10^{-12}$  mol/L (Yang, Tian, Fu, et al., 2024).

## 2.2. Luminol-based ECL system

The Luminol ECL method, discovered in 1929, uses luminol's chemiluminescent properties to emit light (Harvey, 1929). In this process, luminol is mixed with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), which acts as an oxidizing agent, and a catalyst like copper or iron speeds up the reaction. This oxidation generates a blue light, useful for forensic analysis and biochemical assays. Interestingly, mild anodic luminol ECL can occur without H<sub>2</sub>O<sub>2</sub>, but its instability limits the luminol/H<sub>2</sub>O<sub>2</sub> system. Researchers are exploring more stable co-reactants, such as 3-aminophthalhydrazide (TPA) (Sornambigai et al., 2021). Recently, Xia et al. presented luminol-based ECL ultrasensitive and selective detection of aflatoxin B1 (AFB1) using amino-functionalized 3D graphene hydrogel (NGH). In contrast, luminol-palladium-graphene oxide (lum-Pd-GO) acted as the marker for AFB1 antibodies. The mechanistic insights revealed that  $\pi$ - $\pi$  interaction between luminol and GO enhances the ECL signal, making it approximately 8.5 times greater than conventional luminol ECL, led the low detection of AFB1 of  $5 \times 10^{-3}$   $\mu$ g/kg (Xia et al., 2022).

Recently, the catalytic impact of nanoparticles has been demonstrated in luminol-based ECL immunosensors. A microflower-like structure of Co/Ni-MOF nanosheets significantly enhanced ECL efficiency in detecting alpha-fetoprotein. The Co/Ni-MOF structure showed increased surface area, prevented particle aggregation, and exhibited excellent catalytic efficacy. Atomically dispersed cobalt and nickel ions in the ultrathin Co/Ni-MOF played a crucial role in catalyzing the ECL reaction (Wang, Wang, et al., 2020). Further, Zhang et al. explored a luminol-based system featuring a biofunctional Cu-MOF that exhibits enzyme-mimicking activities. This was integrated into an ECL immunosensor through a self-cascade antioxidant reaction. The CuMOF demonstrated superoxide dismutase and catalase activity capabilities and eliminated hydroxyl radicals (OH<sup>•</sup>), showcasing synergistic antioxidant effects and minimal pro-oxidant activities. The nanoconfinement effect provided by layered double hydroxide also ensured a stable ECL signal, which showed variations in response to the target molecule aflatoxin B1 (Zhang, Zhang, et al., 2024).

## 2.3. Nanomaterial-based ECL system

Nanomaterials, which range in size from 1.0 to 100.0 nm in at least one dimension, display unique physical and chemical properties that enhance their electrochemical and optical characteristics. In ECL sensors, these materials serve multiple roles, such as electrode modifiers, aptamer carriers, catalysts, and luminescent reagents. They significantly

boost the sensitivity, specificity, and response time of ECL aptasensors, making them an important area of research for detecting trace substances. Common types of nanomaterials used in this context include noble metal nanomaterials, carbon nanomaterials, quantum dots (QDs), magnetic nanoparticles, and innovative organic nanomaterials (Li, Gao, et al., 2023). Nanomaterial-based electrogenerated ECL systems use the unique properties of nanomaterials to greatly improve ECL signals in biochemical reactions. Researchers are increasingly interested in using nanomaterials such as QDs, silicon, carbon, and metal materials that are helpful to boost ECL sensitivity. The ECL sensing mechanism creates reduced and oxidized species on the electrode surface. Additionally, the co-reactant mechanism involves a reaction between the luminophore and an added reagent. The reaction between the luminophore and reagent results in the electrode potential variation and output signals (Feng et al., 2022; Zhai et al., 2017).

Nanoparticles significantly enhance the available surface area and reactivity in the ECL system with their exceptional physical and chemical properties. A prime example is using covalent organic framework (COFs) composites based on 3-thiophene acetic acid as molecularly imprinted polymer (MIP) materials in ECL sensors. These materials unequivocally demonstrate remarkable ECL behavior when combined with CsPbBr<sub>3</sub> quantum dots and gold nanoparticles (AuNPs) associated with the ligand. The properties of these composites showcase strong ECL characteristics, positioning this platform as an effective sensor for benzo (a)pyrene (BaP). Additionally, the composite's structure provides a substantial specific surface area and optimal imprint recognition sites, further enhancing its functionality (Chi et al., 2023). The success of ECL sensors centers significantly on emission through aggregation-induced emission (AIE), which can cause a spectral overlap in the donor and back hole quencher. In the ECL-RET system, the overlap of spectra with the donor and black hole quencher as the acceptor, upon introducing analytes, will trigger the detachment of BHQ from the electrode surface, thereby leading to the recovery of the ECL signal (Chen et al., 2024).

The success of metal-based materials over conventional single-signal ECL sensors lies in their ability to provide ultra-sensitive and accurate monitoring of food samples. Metallic materials' conducting properties enable them to capture electrons and accelerate chemical reactions at numerous active sites. This acceleration of chemical reactions can improve ECL stability, activity, and the emission of luminophores (Kuang, Li, Chen, et al., 2024). For example, in an electrochemiluminescence assay designed to detect analytes, the integration of gold nanoparticles can dramatically amplify the emitted light signal. This occurs because gold nanoparticles can facilitate electron transfer processes and increase the local concentration of reactive species, thereby enhancing the overall luminescence output. Recently, Yue et al. described europium ion-doped gadolinium trioxide nanocrystals (Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> NCs) as ECL sensors for organophosphorus pesticide detection. An ECL intensity comparison of pure Gd<sub>2</sub>O<sub>3</sub> doped with Eu<sup>3+</sup> ions revealed the intensity of the stable signal even in an analysis of vegetable samples (Yue et al., 2024).

## 2.4. ECL aptamers & immunosensors

ECL aptamers are specialized single-stranded DNA or RNA molecules that exhibit a high affinity for specific target molecules (Song et al., 2024). On the other hand, ECL immunosensors are innovative devices that employ antibodies to selectively detect specific target molecules, providing remarkable specificity and sensitivity. These sensors function by integrating electrochemiluminescence with aptamers or immunoassays (Manzoor et al., 2024). ECL enzyme sensors are designed to monitor biochemical reactions in food products by measuring the electroluminescent signals generated from these reactions. Depending on their core structure, these sensors can function as on-off switches to detect specific analytes in food samples. In a study conducted by Gong et al., a composition was developed that included gold nanoparticles and boron nitride quantum dots (BN QDs) to facilitate the ECL detection of lead

ions ( $\text{Pb}^{2+}$ ). This detection method utilizes the RET effect, which is achieved through the DNzyme cleavage reaction of the substrate chain (Gong et al., 2024).

Consider using hybrid materials as ECL sensors for more accurate and sensitive analysis in food safety. For example, combining  $\text{Ti}_3\text{C}_2$  QDs and 1T/2H  $\text{MoS}_2$ , the resulting nanocomposite aptasensor exhibited improved structural and compositional properties, leading to three times the ECL performance of QDs alone. These hybrid materials functioned as an ECL sensor for extremely low levels of lincomycin in milk. The composition of the material significantly enhanced conductivity and electrocatalytic activity, enabling more precise milk analysis (Du et al., 2024). It has been observed that Zr-MOF exhibited aggregation-induced emission from ligands, acting as high-performance signal modulators by encapsulating ZnS QDs. Meanwhile,  $\text{NH}_2\text{-SiO}_2$  served as ECL quenchers, and ATP biomolecule aptamers functioned as gatekeepers through electrostatic interaction (Li, Xi, et al., 2024). Lv et al. developed an ECL immunosensor for detecting aflatoxin B1 (AFB1) with LOD of 50 fg/mL, using luminol-AgNPs and mesoporous carbon (AgNPs@MC). The sensor was created by modifying a glassy carbon electrode (GCE) with the luminol-AgNPs@MC composite and anti-AFB1 antibodies. This approach of using luminol-AgNPs@MC in immunosensors is advantageous because it enhances sensitivity. During the electrode fabrication, a decrease in ECL intensity was observed, confirming the successful modification of the electrode surface. Electrochemical impedance spectroscopy (EIS) results indicated changes in electron transfer resistance and the diffusion process. Bare electrodes exhibited low electron transfer resistance, while the assembly of anti-AFB1-luminol-AgNPs@MC resulted in an increased electron transfer resistance (Lv et al., 2014).

Table 1 compares food sensors and details the use of ECL materials for food sample analysis. In addition to these materials, MOFs contain metal centers, porosity, and multifunctional sites that allow them to be used for fabrication, immobilization, and composition with metal and nonmetallic ECL active materials. This hybridization results in an advanced structural platform for analysis applications. The hybrid MOFs enable accelerated chemical reaction signal generation through electron conduction.

### 3. MOF design and signal generation mechanism

#### 3.1. MOFs design

MOFs are considered advanced materials due to metal and organic moieties, porosity for loading various entities, multifunctional

interaction sites, and large surface area for electrode formations (Liu et al., 2019). A diverse array of ligands and linkers are employed in synthesizing MOFs. These encompass carboxylate ligands ( $-\text{COOH}$ ) with robust metal ion coordination, nitrogen-containing ligands like pyridine or imidazole derivatives, and phosphonate linkers known for their strong metal coordination properties (Lin et al., 2023; Luo, Fu, et al., 2023; Wang, Gu, et al., 2023). Furthermore, various MOF architectures with distinctive properties and applications are developed using additional ligands such as bipyridine, terpyridine, and benzene-1,4-dicarboxylate. Several techniques, including solvothermal, hydrothermal, microwave-assisted, mechanochemical, electrochemical, and layer-by-layer assemblies, are routinely used to design and synthesize MOFs (Sun, Qin, et al., 2023; Yuan et al., 2023; Zhai et al., 2023). Additionally, advancements in methods such as spray pyrolysis, vapor phase processes, mechanochemical approaches, templating techniques, hybrid methods, and crystal engineering have been leveraged to shape MOFs into highly efficient platforms (Fig. 3) (Chen, Gliemann, & Wöll, 2023; Guo et al., 2024). These methods can change the physicochemical properties of MOF derivatives. For example, pyrolysis involves the high-temperature decomposition of organic ligands, forming metal oxides. Sulfuration creates metal sulfides, while phosphorization modifies the electronic structure of the materials. Selenylation results in the formation of distinct metal selenides. Understanding these relationships is essential for customizing materials with specific functionalities, which contributes to scientific advancements and the innovative applications of MOFs (Fu et al., 2023; Wang, Gao, et al., 2023). Controlling the crystalline orientation of MOF pore channels can lead to anisotropic properties and enhanced diffusion (Linares-Moreau et al., 2024). The relationship between the various preparation methods used for MOF derivatives and their physicochemical properties plays a critical role in enhancing ECL sensing applications. Understanding how different synthesis techniques influence properties such as surface area, porosity, and chemical stability is vital for optimizing the performance of MOFs in ECL sensors. By tailoring these preparation methods, researchers can develop MOF derivatives that exhibit improved sensitivity and selectivity in detecting target analytes, thereby advancing the capabilities of ECL sensing technologies (Dai et al., 2023; Zhao, Wang, Wang, Fan, et al., 2023).

Recently, Zr-MOFs have been designed with model support for uniform arrays that feature MOF-node-grafted metal-oxy and metal-sulfur clusters. These MOFs possess 12 connected unoccupied sites, which could be effectively utilized for various applications (Lu et al., 2020). It can be observed that MOFs have shown that they can alter the oxidation states of their metal parts when subjected to an outside influence. This

**Table 1**  
ECL sensing materials and their analytical performances for food samples analysis.

| Materials   | Analytical                  | LOD/<br>Sensitivity     | Linear range                                   | Mechanism insights   | Sample source                 | Ref.                            |
|---|-----------------------------|-------------------------|--|--|-------------------------------|---------------------------------|
| CdSe@ZnSe and CNTs  | melamine                    | $3.3 \times 10^{-12}$ M | $1.0 \times 10^{-11}$ – $1.0 \times 10^{-7}$ M | co-R & ER; Ru(bpy) $_3^{3+}$ and TPrA adsorption onto the electrode led oxidized to products   | milk                          | (Wu et al., 2024)               |
| COF-300-Au-based MI   | BaP                         | $4.1 \times 10^{-15}$ M | $10^{-14}$ to $10^{-5}$ M                      | co-R & ER; oxidation of quinones generated followed ECL quenching through energy transfer  | Soybean, rapeseed & olive oil | (Chi et al., 2023)              |
| Pdots   | As(III)                     | 5.8 pM/0.4 ppt          | 10 pM to 500 nM                                | overlap of spectra employed ECL-RET system   | rice grain                    | (Chen et al., 2024)             |
| $\text{Mn}_2\text{SnO}_4$ nanocubes                           | RBV                         | 0.85 ng/mL              | 1–2000 ng/mL                                   | co-R & ER; luminophores $\text{Mn}_2\text{SnO}_4$ ECL emission in the co-reactants $\text{K}_2\text{S}_2\text{O}_8$ presence   | milk and chicken              | (Kuang, Li, Chen, et al., 2024) |
| $\text{Gd}_2\text{O}_3\text{:Eu}^{3+}$ NCs                    | organophosphorus pesticides | 0.12 pM                 | 1 nM to 1 pM                                   | co-R & ER; $\text{Eu}^{3+}$ ions caused enhanced ECL, $\text{H}_2\text{O}_2$ quenched the ECL intensity  | vegetable samples             | (Yue et al., 2024)              |
| AuNPs- BN QDs   | $\text{Pb}^{2+}$            | $2.6 \times 10^{-13}$ M | $10^{-12}$ – $10^{-5}$ M                       | co-R & ER; RET effect between AuNPs and BN QDs and the recognition of $\text{Pb}^{2+}$   | Water                         | (Gong et al., 2024)             |
| $\text{Ti}_3\text{C}_2$ QDs-1 T/2H $\text{MoS}_2$ nano-hybrid | lincomycin                  | 0.02 ng/mL              | 0.05 ~ 100 $\mu\text{g/mL}$                    | co-R & ER; first electrochemical reduction, then reduction of co-reactant, and transforming by the electron-transfer annihilation between $\text{Ti}_3\text{C}_2$ QDs $^{*-}$ 1T/2H $\text{MoS}_2$ and $\text{SO}_4^{*}$ | Milk                          | (Du et al., 2024)               |

Covalent organic framework composite (COFs), Molecularly imprinted (MI), polymer dots (Pdots), europium ion-doped gadolinium trioxide nanocrystals ( $\text{Gd}_2\text{O}_3\text{:Eu}^{3+}$  NCs), boron nitride quantum dots (BN QDs), benzo(a)pyrene (BaP), ribavirin (RBV), CO-reactant (co-R), electron redox (ER), resonance energy transfer (RET)

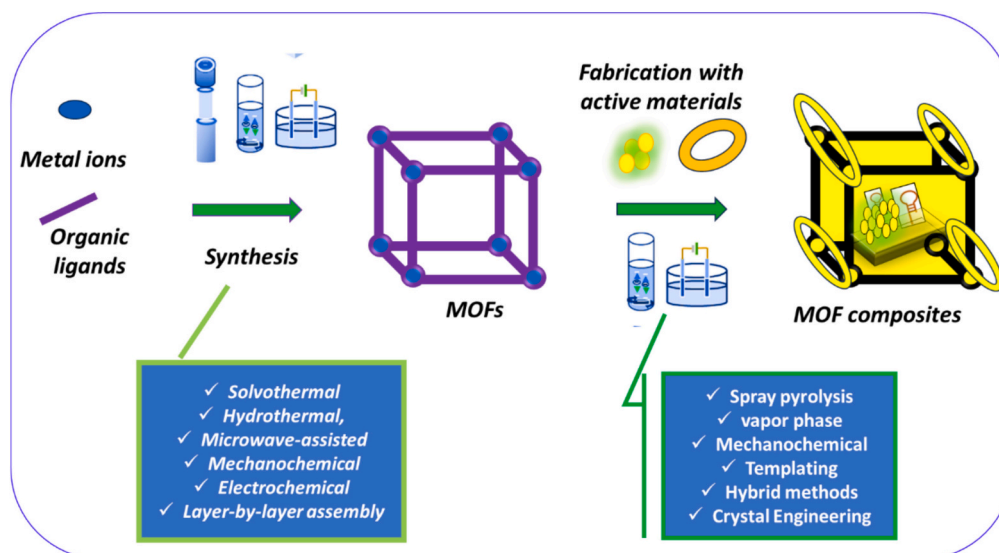


Fig. 3. A schematic representation of MOF design and fabrication for developing an efficient platform.

transformation happens as the linker photoisomers switch between +2 and +1 oxidation states. This distinct quality allows the MOF to display improved conductivity, cyclic voltammetry, and electronic magnetic properties (Martin et al., 2022). Anemone-like Cu-MOFs loaded with AuPd nanoparticles and polyethyleneimine-reduced graphene oxide/AuAg nanosheet composites (PEI-rGO/AuAg NSs) have a large surface area and excellent electrical conductivity. This allows for efficient detection of T-2 toxin (T-2). The modified MOF, combined with nanomaterials and graphene oxide, acts as a triple helix molecular switch and enables signal amplification by a swing-arm robot (Zhang et al., 2023). When developing MOF ECL sensors for food analysis applications, utilizing multifunctional ligands and employing a suitable synthetic approach is imperative. Carefully selecting ligands with multiple functional groups is essential for achieving high sensitivity and selectivity in detecting target analytes in complex food samples. Also, choosing a well-suited synthetic approach is crucial to ensure the precise formation of MOF structures that exhibit optimal electrochemical and optical properties for effective sensing in food analysis.

### 3.2. Signal generation mechanism

ECL is an advanced transduction technique known for its high power level and strong outcome signals. The efficiency of ECL generation depends on various factors, including the materials used in the process, such as luminophores and co-reactants (Giagu et al., 2024; Zanut et al., 2021). These materials are essential for improving ECL's overall performance and effectiveness. It is undeniable that ECL is a potent transduction technique, and the signal strength relies on the overall efficiency of the mechanisms involving redox luminophores or co-reactants (Qi & Zhang, 2020; Zanut et al., 2020). The ECL phenomenon can be caused by various chemical systems, including materials such as  $\text{Ru}(\text{bpy})_3^{2+}$  and luminol, as noted by luminophores. The understanding of mechanistic insights can differ based on the size, geometry, and emission properties. One of the most common ECL mechanisms is based on  $\text{Ru}(\text{bpy})_3^{2+}$  and its derivatives due to their excellent photochemical properties. The common route for ECL signals involves three steps:  $\text{Ru}(\text{bpy})_3^{3+}$  and TPrA as co-reactants, the oxidative-reduction route, and electrochemical oxidation into  $\text{Ru}(\text{bpy})_3^{3+}$  and  $\text{TPrA}^{\bullet+}$ . The process is followed by the conversion of  $\text{TPrA}^{\bullet+}$  to  $\text{TPrA}^{\bullet}$ , a strong reducing radical intermediate formed by losing a proton. In the next step,  $\text{Ru}(\text{bpy})_3^{3+}$  converts to  $\text{Ru}(\text{bpy})_3^{2+*}$ , which is responsible for light emission (Rebeccani et al., 2022; Zanut et al., 2020).

Another mechanism route involves a luminol-based ECL system for

signal generation. This mechanism, based on the luminol/ $\text{H}_2\text{O}_2$  system, follows two common routes (Sun, Cheng, et al., 2023). First,  $\text{H}_2\text{O}_2$  can be electrochemically oxidized and then trigger ECL reactions involved in electrode reactions acting as co-reactants and oxidants to oxidize subsequent reagents. Also,  $\text{H}_2\text{O}_2$  is an oxidant with electrochemical oxidative production of luminol responsible for ECL signals.  $\text{H}_2\text{O}_2$  as a co-reactant and electrochemical oxidation into superoxide anion radical ( $\text{O}_2^{\bullet-}$ ) enriches the environment with radicals that react with intermediates to generate excited 3-amino phthalate and finally emit blue fluorescence (425 nm). Two-step electron loss processes lead to deprotonated  $\text{H}_2\text{O}_2$  that reacts with products of luminol after two-step electron loss processes (Zhou et al., 2022). Additionally, nanomaterial-based ECL systems benefitting from the emission wavelength and quantum size effect showed electrochemical and optical properties (UV to NIR region) with advantages of large Stokes shift and long lifetime fluorescence (Nikolaou et al., 2021). In brief, MOFs ECL food sensors work on a Luminol-based system, catalyzing the co-reaction, Oxidative-reductive, and Hybridization chain reaction system. The possible physical and chemical properties transformations due to different electrostatic, hydrogen,  $\pi$ - $\pi$  stacking bonding, and molecular forces could be read out in output signal forms (Fig. 4) (Guo et al., 2023; Lai et al., 2023; Mehta et al., 2023).

Therefore, optimizing materials with MOFs can adopt any strategies based on  $\text{Ru}(\text{bpy})_3^{3+}$ , luminol, and nanomaterials (Jiang et al., 2024; Ma et al., 2024). MOF materials can adopt aggregation-induced emission (AIE)-active strategies, introducing donor-acceptor (D-A), resonance energy transfer-active moieties for ECL-based analytes monitoring. The incorporation of  $\text{Ru}(\text{bpy})_3^{3+}$ , luminol, and nanomaterials as intrinsic luminescent ctenophores provides an ideal ECL-active MOFs. MOFs' micro and nanoscale porosity and tuned structure allowed various inorganic and organic materials for composition. Also, porphyrins and derivatives provide ECL activity due to unique molecular structures and electronic properties (Zhou et al., 2020). MOFs immobilized with photosensitive materials like inorganic semiconductors (e.g., ZnO), polyaniline, and methylene blue (MB) play key roles in light and electrical signal management through their donor and acceptor sites. ECL processes can involve signal enhancement and quenching. In NGQDs- $\text{Ru}@\text{SiO}_2$ , the ECL emission results in a shorter electron transfer distance. Here,  $\text{Ru}(\text{II})$  is oxidized to  $\text{Ru}(\text{III})$  as NGQDs release an electron to form  $\text{NGQDs}^{\bullet+}$ . These charged NGQDs donate a proton to convert back to  $\text{NGQDs}^{\bullet}$ , allowing  $\text{Ru}(\text{III})$  to revert to  $\text{Ru}^*(\text{II})$ , which then emits light at 625 nm. The quenching efficiency of MB differs between  $\text{NGQDs-Ru}@\text{SiO}_2$  and  $\text{Ru}@\text{SiO}_2$ , with  $\text{NGQDs-Ru}@\text{SiO}_2$  showing greater

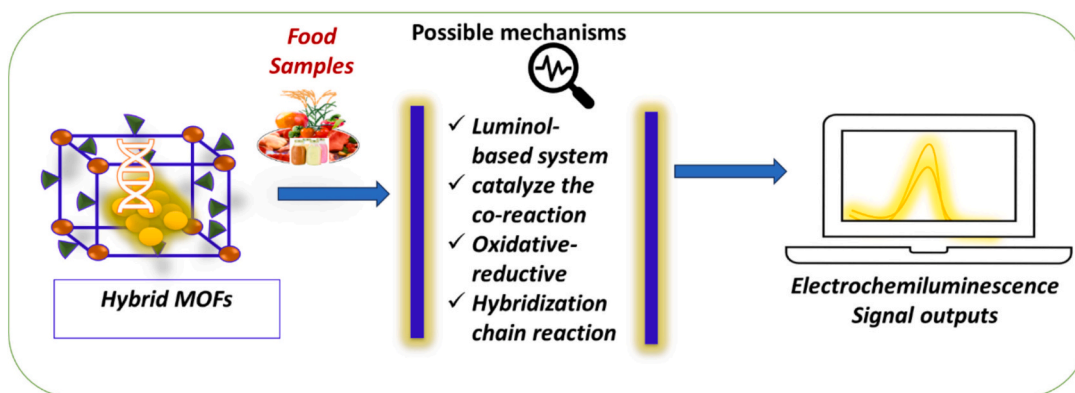


Fig. 4. The schematic representation of MOFs ECL food sensors with mechanistic insights.

quenching (Fig. 5) (Liu et al., 2023).

Photosensitive material based on these systems efficiently converts light energy into electrical signals. Following this approach, donor sites

act as electron suppliers for photosensitive material, a backup that outputs stable photocurrent (Liu, Dong, et al., 2024). For example, a hollow copper-cobalt MOF (Cu/Co-MOF) was loaded with luminol to

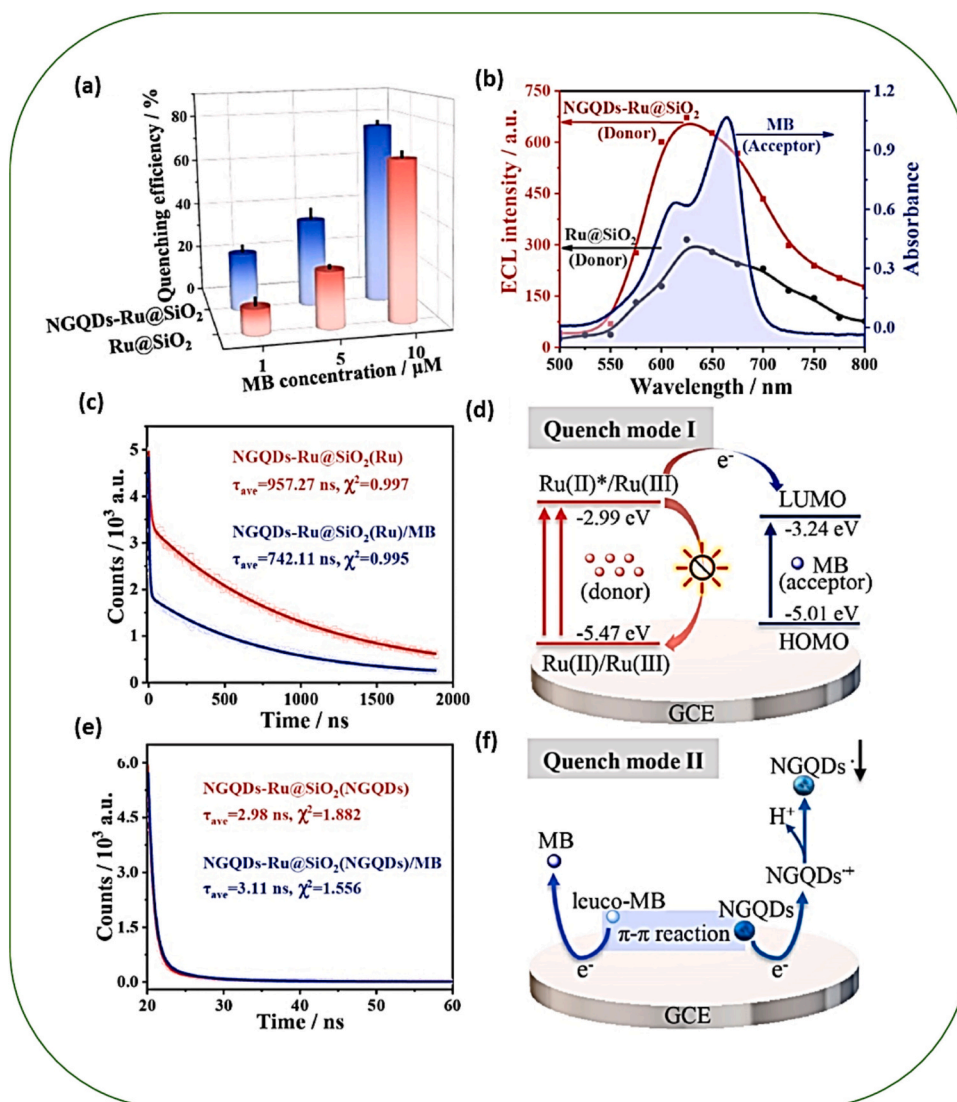


Fig. 5. (a) Ru@SiO<sub>2</sub> and NGQDs-Ru@SiO<sub>2</sub> quenching efficiency with varying concentrations of MB. (b) ECL spectra and UV-Vis absorbance of MB for Ru@SiO<sub>2</sub> and NGQDs-Ru@SiO<sub>2</sub>. (c) NGQDs-Ru@SiO<sub>2</sub> (Ru) time-resolved photoluminescence decay with and without MB. (d) Proposed quenching mechanism between the luminophore and MB. (e) NGQDs-Ru@SiO<sub>2</sub> (NGQDs) time-resolved photoluminescence decay with MB. (f) Proposed quenching mechanism between the co-reactant and MB. Reproduced with the permission of (Luo, Liu, et al., 2023) © 2022 Elsevier B.V. All rights reserved.

obtain an efficient ECL platform. Luminol significantly catalyzes  $\text{H}_2\text{O}_2$  to produce more  $\text{O}_2$ , enhancing ECL signals and efficient analysis of acetamiprid and malathion in apple and tomato samples. The observed ECL-potential curves of electrodes need work in a particular potential range for strong ECL strength in bare and combined with nanomaterials to inject electrons through conduction bands (Liu et al., 2021). It can't be denied that variations in electrical and optical activities significantly impact the outcomes and analysis of standard electrochemical and optical techniques. ECL has surged as an exceptionally robust analytical technique to counter these challenges, leveraging its dual electrochemical and luminescence properties alongside additional ECL luminophores. ECL-based analysis can seamlessly integrate with other methods, yielding a highly adaptable sensing platform. The integration of novel materials like nanomaterials, metal and organic frameworks, and covalent frameworks has led to the development of highly effective ECL sensors for analyzing ecological, food, and clinical samples, employing immunoassay and aptasensor strategies (Hao & Wang, 2016).

#### 4. ECL MOF food sensors

MOF materials are promising candidates for analyzing food samples due to their high and uniform porosity, large surface areas, low density, customizable structures, and polar sites (Gao et al., 2024; Liu, Mu, et al., 2024; Sun et al., 2024; Zhang, Han, et al., 2024). In addition, MOFs are promising hosts for various guest analytes through diverse grafting groups. MOFs can be modified by in-situ modification and fascinating sensing and adsorption characteristics. MOFs' high crystalline and permanent porosity allowed them to interact with different analytes through a significant change in their conductive, optical, catalytic, mechanical, and other properties, which can be observed in signal transductions. MOFs are suitable for promoting electrochemically generated intermediates suitable for ECL exergonic reaction for light emission upon relaxation to a lower energy state (Pan et al., 2024).

##### 4.1. Mycotoxins detection

Mycotoxins are harmful substances produced by certain fungi that can contaminate food and feed, posing a threat to human and animal health (Moghadas et al., 2024; Ozel & Karaca, 2024). One innovative method for detecting these mycotoxins is through ECL using MOFs. MOFs are porous materials with high surface areas, making them ideal for capturing and detecting mycotoxins. The ECL technique can accurately detect and quantify these toxins in food samples by functionalizing MOFs with specific receptors that bind to aflatoxins. Moreover, using MOFs in ECL detection offers advantages such as high sensitivity, rapid response, and low detection limits. These characteristics make this method a promising tool for screening mycotoxin contamination in various food products (Han et al., 2024).

Wang et al. constructed methylamine perovskite (MP) QDs loaded ZIF-8 for AFB1 ECL tracing with a LOD of 3.5 fg/mL. ZIF-8, with a confined cavity structure, provided a platform for MP QDs loading that helped achieve stable and robust ECL signals. The GCE with MP QDs@ZIF-8 composites was performed for AFB1 detection using 0.1 M TPrA as the co-reactant. MP QDs@ZIF-8 ECL peak centered at 554 nm showed a redshift of 26 nm due to triggered electrons relaxation or hole injections that lead. In addition, potential scanning MP QDs@ZIF-8/GCE and MP QDs/GCE were applied, and they showed an anodic peak  $\sim$ of 1.4 V, attributing to the electrogenerated oxidized species. The real sample analysis of corn samples at different concentrations of AFB1 showed recoveries of 107.0 %, 106.0 %, and 107.0 %, respectively, with precision ranging from 4.8 % to 7.1 % and 5.6 % to 9.7 %. The proposed electron and proton transfer mechanism follows the MP QDs@ZIF-8 to MP QDs<sup>+</sup>@ZIF-8 with electron loss, then TPrA to TPrA<sup>•+</sup> with electron loss, and TPrA<sup>•+</sup> with proton loss. Further, the MP QDs@ZIF-8 and TPrA<sup>•+</sup> convert to MP QDs-@ZIF-8; in the next step, MP QDs<sup>+</sup>@ZIF-8 and MP QDs-@ZIF-8 form an excited state for MP QDs\*@ZIF-8 that responsible

for ECL emission (Fig. 6) (Wang, Xiong, et al., 2023).

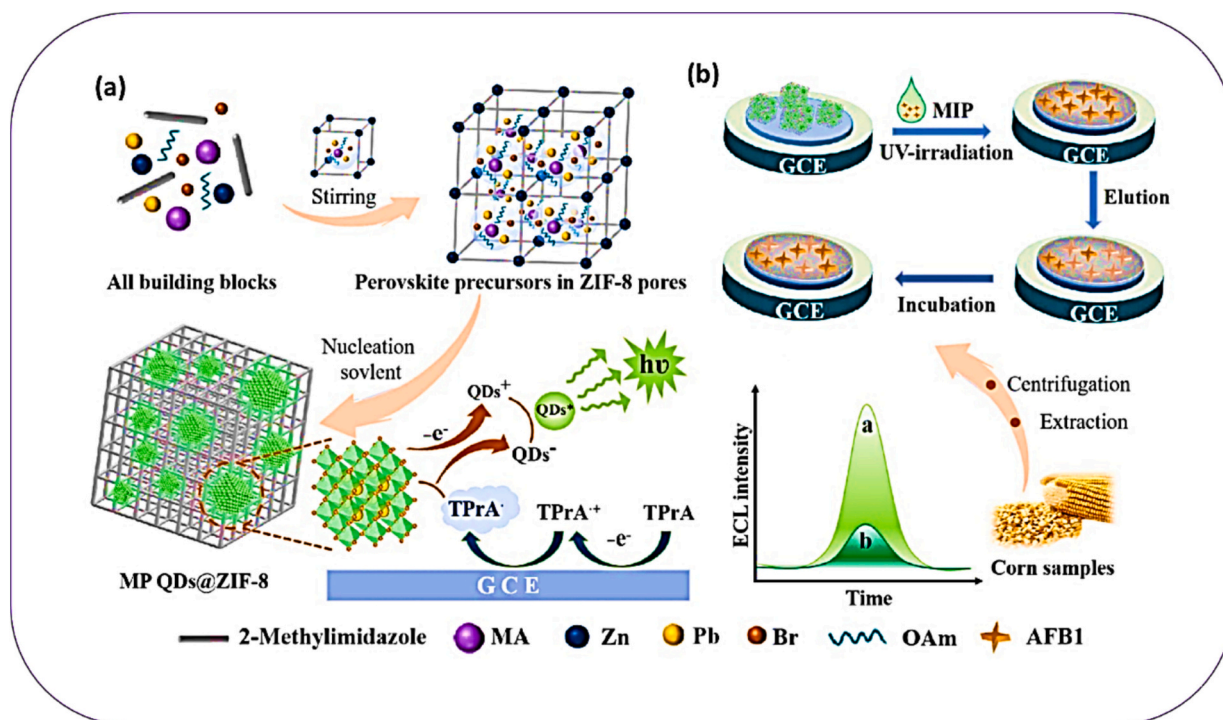
Huang et al. developed a dual-mode paper chip (DPC) ECL sensor using UiO-66-NH<sub>2</sub>. The sensor featured a patterned paper electrode and a colorimetric region treated with platinum nanoparticles for dual-mode outputs. The UiO-66-NH<sub>2</sub> was loaded with 3,3',5,5-tetramethylbenzidine (TMB) and controlled by a switch made up of CdS quantum dots-aptamer. When the target contaminant AFB1 was present, the MOF ECL sensor induced the release of TMB, enabling ultra-high sensitivity with a detection limit of 7.8 fg/mL, even in real corn samples. The performance of DPCs with an aptamer-gated TMB release system demonstrated dual-mode AFB1 detection through colorimetric and ECL signals. The AFB1-Apt-CdS on the ECL area and the released TMB small molecules reached the Pt NPs-treated colorimetric area for precise quantification of AFB1 level by portable DPCs (Fig. 7) (Huang et al., 2024).

##### 4.2. Bacteria detection

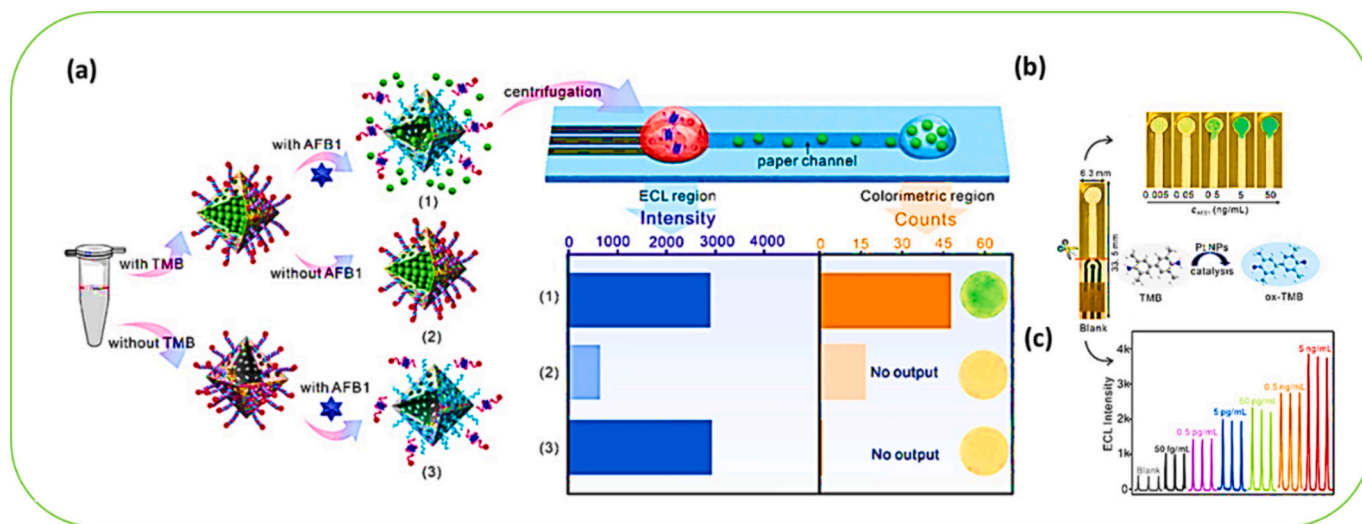
The detection of bacteria using MOF ECL sensors has emerged as a promising technique in biosensors and food chemistry. MOFs, which have tunable properties, play a crucial role in enhancing both the sensitivity and selectivity of bacterial detection. For example, researchers have successfully combined MOFs with specific antibodies to target bacterial cell surface markers, allowing for the rapid and accurate identification of harmful bacteria in various samples. Additionally, the unique structure of MOFs enables the immobilization of enzymes or other biomolecules, which improves detection efficiency by amplifying the ECL signal when interacting with bacteria. This approach provides a method for real-time monitoring of bacterial contamination in food, water, and clinical samples (Li et al., 2016; Wu et al., 2025).

*Staphylococcus aureus* is a pathogen that causes health hazards. It has developed a two-component system that makes it more resistant to antimicrobial drugs (Firyal et al., 2019). Zhai et al. studied the use of ECL sensing to detect lead (Pb(II)) and *Staphylococcus aureus* (S.aureus) by employing Au@Ni-Co-MOFs. The authors developed a sensitive MOF ECL platform using Au@luminol and Cadmium sulfide (CdS) QDs with improved surface area and catalytic sites. Their research revealed that the urchin-like Au@luminol-DNA2 aptamer recognized Pb(II) through Au-S bonding. In contrast, the CdS QDs-DNA3 aptamer showed specificity in recognizing S.aureus through catalyzed hydrogen peroxide reduction for ECL signals. They also provided insights into the mechanism, indicating that ECL biosensors Au@Ni-Co-MOFs catalyze the co-reaction buffer  $\text{H}_2\text{O}_2$ , resulting in the formation of  $\text{HO}_2^\bullet$  and  $\text{O}_2^{\bullet-}$ . The study demonstrated the use of luminol in electrocatalysis to produce free radicals and reduce CdS QDs to form CdS QDs<sup>•-</sup> through current excitation. ECL signals showed energy is released when the excited substance returns to the ground state. The authors designed a MOF-based analysis model to detect Pb(II) and S in scallops and fish aquatic products, with promising recoveries of 95.65 % –115.43 % and RSDs of 0.4 %–2.17 % (Zhai et al., 2024).

The controllable properties of ECL MOF sensors allow for customization according to specific requirements, enabling researchers to tailor the sensor's performance to suit their needs. With ongoing advancements in technology and material science, ECL MOF sensors have an increasingly important role in analytical and sensing applications (Nie et al., 2023). Several amplification strategies, such as enzyme-based methods, polymerase chain reaction (PCR), rolling circle amplification (RCA), loop-mediated isothermal amplification (LAMP), and strand displacement amplification (SDA), have been established for food safety and environmental monitoring (Liu et al., 2023; Mohsen & Kool, 2016; Yao et al., 2021; Zhang, Liu, et al., 2021). In addition to enzyme-based amplification, non-enzymatic approaches have emerged as promising signal enhancement alternatives. However, signal amplification strategies face challenges such as background noise, nonspecific binding, and interference from complex matrices (Chen, Lan, et al., 2023; Xu et al., 2021). To overcome these issues, various MOF materials-based



**Fig. 6.** Schematic representation for the MPQDs@ZIF-8-based molecular imprinting that showed ECL intensity and was used for the detection of AFB1 in corn samples. (a) Synthesis of MPQDs@ZIF-8 and proposed ECL reaction, electron-proton transfer mechanism. (b) observed signal changes and responses of the ECL sensor to detect AFB1. Reproduced with the permission of (Wang, Xiong, et al., 2023) © 2022 Elsevier Ltd. All rights reserved.

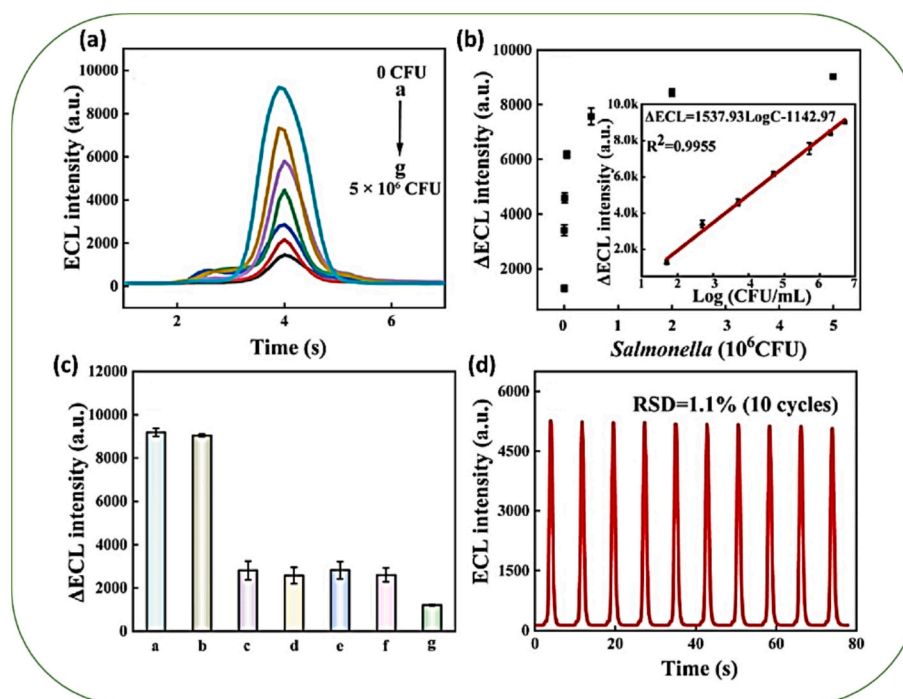


**Fig. 7.** (a) Feasibility of proposed Paper Chips (DPCs) for AFB1 detection: Top: sDNA/UiO-66-NH<sub>2</sub> loading with TMB for 0.5 ng/mL AFB1 detection. Middle: no AFB1 target as a blank. Bottom: sDNA/UiO-66-NH<sub>2</sub> loading without TMB for 0.5 ng/mL AFB1 detection. (b) Colorimetric photos of DPCs for detecting various AFB1 standard concentrations. (c) A portable ECL detector analyzed ECL signals of DPCs for different AFB1 concentrations. Reproduced with the permission of (Huang et al., 2024) © 2024 Elsevier Ltd.

strategies have been promising to improve the selectivity and sensitivity of signal amplification (Zhu et al., 2023). For example, Wang et al. report Zr-MOF ECL sensor based on signal amplification strategy using bio-recognition element and CRISPR/Cas12a probe for the detection of *Salmonella* with LOD of 37 CFU/mL and linear range of 50 CFU/mL to  $5 \times 10^6$  CFU/mL through signal amplification strategy. The structure switching occurs in the presence of *Salmonella* on allosteric probes, which leads to hybridization with primers to trigger isothermal amplification. CRISPR-gRNA subsequently recognized the release of *Salmonella* to initiate a reaction by dsDNA generation in the trans-cleavage of

Cas12a following the electrode-bounded ssDNA cut for releasing ECL emitter porphyrinic Zr-MOF (PCN-224) and quenching in ECL signals. The designed MOF ECL sensor showed physical applicability to detect *Salmonella* in milk samples with a recovery range of 107.8 % to 113.4 % (Fig. 8) (Wang, Zhang, et al., 2023).

Wei et al. developed a Faraday cage-type aptasensor for the dual-mode detection of *Vibrio parahaemolyticus* (VP). This sensor utilized electrogenerated ECL with a Pb<sup>2+</sup>-Ru-MOF@Apt2 as the signal unit. The authors demonstrated that Apt2 specifically recognizes VP, leading to the generation of both ECL and differential pulse voltammetry (DPV)



**Fig. 8.** (a) ECL signal intensity and changes with increasing *Salmonella* concentration [a (0 CFU/mL), b, c, d, e, f, and g (5 × 10<sup>1</sup>, 10<sup>2</sup>, 10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup>, and 10<sup>6</sup> CFU/mL)]; (b) ECL signal intensity and *Salmonella* concentration linear relationship; (c) Histogram for the specificity test: [(a) *S. enteritidis* (CMCC 50335), (b) *S. enteritidis* (CMCC 50041), (c) *L. gasseri*, (d) *E. coli*, (e) *H. pylori*, (f) *S. aureus*, (g) PBS]. The bacterial concentration is 1 × 10<sup>6</sup> CFU/mL; (d) Stability test under 10 consecutive cyclic potential scans. Reproduced with the permission of (Wang, Zhang, et al., 2023) © 2023 Elsevier Ltd. All rights reserved.

signals. The Ru-MOF layered on the electrode, facilitated electron exchange and enhanced sensitivity. The dual-mode detection method demonstrated improved accuracy and reliability while maintaining satisfactory stability and selectivity, ensuring food safety in the analysis of real seafood samples. In this setup, Ru-MOF acted as the ECL signal tag, and Pb<sup>2+</sup> served as the electrochemical signal tag, simplifying the signal tags' assembly process. Additionally, thiol-modified Apt1 captured VP on the gold electrode, while Apt2 assembled the signal unit on the VP, further enhancing the signal intensity (Wei et al., 2020).

#### 4.3. Insecticides/pesticides detection

Electrogenerated ECL is a powerful technique that has gained popularity for detecting insecticides and pesticides. MOFs are tailored for specific applications, offering advantages such as small size and excellent chemical stability. ECL MOF sensors, which incorporate luminol, aptamers, and Ru(bpy)<sub>3</sub><sup>2+</sup> along with its derivatives, are well-studied for their luminescent properties. To achieve a strong ECL signal, co-reactants like oxalates and tris(2-carboxyethyl)phosphine (TPrA) are necessary (Wang, Ding, et al., 2023; Yan et al., 2019).

Heterostructure MOF materials are allowed to trap different molecules inside it due to material interaction with each other through various interactions. Due to this, MOF materials acted as a container for capturing various molecules through  $\pi$ - $\pi$  interactions and hydrogen bonding that trigger an aggregation-induced emission (AIE) effect (Yang, Zhou, Wang, et al., 2024). Liu et al. designed a Eu<sup>3+</sup>-MOF-253@Au ECL sensor to detect carbaryl with LOD of 0.14  $\mu$ g/L in the 0.2–200  $\mu$ g/L range. The Au NPs embedded inside Cu-MOF pore channels provided a solution for enhancing catalytic activity to confer the ECL performance. Eu<sup>3+</sup>-MOF-253@Au actively catalyzed carbaryl into 1-naphthol, and ECL signals were quenched. The real sample analysis for carbaryl in milk and soybean oil showed recoveries of 76.5–95.4 % (Liu et al., 2022).

The ECL MOF sensors have great electrochemistry and chemiluminescence features that allow precise control, high sensitivity, and

minimal background noise. Fang et al. recently designed a sensor based on gold-copper doped Tb-MOFs (Au@Cu:Tb-MOFs) for detecting chlorpyrifos (CPF) at ultra-trace levels, with a LOD of 0.029 pg/mL in the range of 0.1–106 pg/mL. The authors modified the electrode systematically with 4,7-bis(thiophene-2-yl)benzo[c][1,2,5]thiadiazole and chlorpyrifos through electropolymerization on the electrode surface to form MIP. The MIP enabled specific target analysis, validated with molecular docking through  $\pi$ -alkyl interaction. It was observed that the MIP film with 4,7-bis(thiophene-2-yl)benzo thiadiazole enhances sensitivity, while the Au@Cu:Tb-MOFs promote co-reaction for ECL emission signal for CPF detection (Fang et al., 2024).

Liu et al. designed a hollow Cu/Co-MOF that was further loaded with luminol to catalyze the decomposition of H<sub>2</sub>O<sub>2</sub>, resulting in an increased production of O<sub>2</sub><sup>2-</sup> and enhanced ECL signals. This setup was utilized to detect acetamiprid and malathion, achieving LODs of 0.015 pM and 0.018 pM, respectively, within a concentration range of 0.1  $\mu$ M to 0.1 pM. Additionally, luminol and graphite-like carbon nitride nanosheets (g-C<sub>3</sub>N<sub>4</sub>) were employed to develop dual ECL signal sensors operated at −1.5 V and 0.6 V. In the analysis of real samples, 100 g of tomato and apple samples were broken down and dispersed in 0.1 L of 0.2 M phosphate-buffered saline (PBS) at pH 7.4. The results showed a relative standard deviation (RSD) of less than 4.28 %, with recoveries of 94 % for acetamiprid and 102 % for malathion detection. (Liu et al., 2021). ECL MOF sensors have been successfully applied for the analysis of pesticide residues in Chinese herbal medicines (CHMs) to address growing concerns. Li et al. developed an aptasensor for the trace detection of acetamiprid (ACE) in *Angelica sinensis* and *Lycium barbarum*. This sensor utilized UiO-66 modified with amino groups, and gold nanoparticles (AuNPs) facilitated the catalysis of excited states of luminescent molecules by UiO-66-NH<sub>2</sub>. The designed model showed LOD of 0.8 pM as superior to traditional fluorescence detection methods. The mechanistic insight revealed that charge transfer resistance (R<sub>ct</sub>) increased progressively after modifying the electrode with AuNPs@UiO-66-NH<sub>2</sub>, followed by aptamer. Furthermore, the ECL strength improved with Ru (bpy)<sub>3</sub><sup>2+</sup> and multi-walled carbon nanotube (MWCNT) nanocomposites

but decreased after adding AuNPs@UiO-66-NH<sub>2</sub>, the aptamer, and subsequently BSA (Fig. 9) (Li et al., 2025).

#### 4.4. Pharma and industrial residues detection

Detecting insecticides through ECL using MOFs is an innovative research area in food sample analysis. MOFs are ideal for sensing applications that selectively detect specific insecticides in complex samples. Functionalizing the MOF surface with molecules and ECL as a detection method offers high sensitivity and selectivity, making it suitable for trace-level analysis of insecticides. This technique relies on light generation through electrochemical reactions, quantitatively measuring the insecticide concentration. MOFs offer exceptional selectivity, rapid response time, and cost-effectiveness for analyzing food safety and quality, making them the ideal choice for sample analysis (Lei, Yin, et al., 2024; Xu et al., 2024). Liu et al. developed a signal-on aptasensor using a combination of AuNPs, double-stranded DNA (dsDNA), and Ce-MOF for susceptible detection of sulfadimethoxine (SDM) through the aptamer-SDM complex, causing the dsDNA to dissociate. The ECL signals increased after the release of the aptamer due to the combination of the capture probe (CP) with the tracer label. The designed aptamer demonstrated an ultra-trace detection limit of 1.28 fg/mL within a linear response range from 10.0 fg/mL to 100 ng/mL for SDM detection, even when applied for analyzing real milk samples. The results from cyclic voltammetry (CV) and ECL responses revealed that the bare GCE in phosphate-buffered saline (PBS) showed neutrality and exhibited no redox peak. The reduction peak of 1,3,6,8-tetra(4-carboxyphenyl) pyrene (H<sub>4</sub>TBAPy) linked Zn-TBAPy-MOF (ZPM) in PBS shifted with the introduction of co-reactant K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Real sample analysis demonstrated the reliability of the MOF ECL aptasensor in detecting SDM in milk samples. Samples showed 97.9 % to 107 % recoveries with a relative standard deviation (RSD) of 1.75 % to 4.21 % (Fig. 10) (Liu et al., 2023).

Shan et al. designed a Ru@Zn-MOF/nafion modified GCE ECL sensor for the detection of brilliant blue FCF (BB) with LOD of  $2.5 \times 10^{-8}$  M. Zn-MOF immobilized with Ru(bpy)<sub>3</sub><sup>2+</sup> in solution phase differ from conventional solid. Ru@Zn-MOF/nafion exhibited significant quenching ECL intensity after adding BB as evidence of interactions. The observed

ECL quenching in Ru@Zn-MOF/nafion/TEA intensity could be due to the redox reaction, i.e., Ru(bpy)<sub>3</sub><sup>2+</sup> and TEA oxidized electrochemically to Ru(bpy)<sub>3</sub><sup>3+</sup> and TEA<sup>•+</sup>, then  $\alpha$ -deprotonation to form TEA<sup>•</sup> radical. The formed radical TEA<sup>•</sup> could radical Ru(bpy)<sub>3</sub><sup>3+</sup> to Ru(bpy)<sub>3</sub><sup>2+•</sup>, responsible for ECL signals generation by radiative de-excitation. At the same moment, iminium ions formed to reduce TEA. The formed TEA<sup>•</sup> radicals could be consumed in redox for BB detection, responsible for quenching ECL intensity (Shan et al., 2019).

Wang et al. designed MOFs using Fe TCPP(Zn) with homogeneous catalytic sites. They utilized ferric-based metal ligands as co-reaction accelerators, which improved the efficiency of converting H<sub>2</sub>O<sub>2</sub> on the MOFs' surface and increased the concentration of <sup>•</sup>OH for self-enhanced ECL. They constructed an aptasensor for the specific detection of kanamycin (KAN) using Fe TCPP(Zn) MOFs as donors and AuNPs as acceptors, achieving a detection limit of 0.28 fM. This innovative ECL strategy expands MOFs' applications to trace antibiotics analysis in food and the environment (Wang et al., 2024). The study investigated the impact of self-enhancement by recording ECL intensities of different MOFs in H<sub>2</sub>O<sub>2</sub>. The ECL emissions of Zn TCPP MOFs (curve a) and Fe TCPP MOFs (curve b) were weak, while Fe/Zn TCPP MOFs (curve c) exhibited significant ECL signals. Fe TCPP(Zn) MOFs (curve d) displayed ECL strength three times higher than Zn TCPP MOFs (Fig. 11a). The process illustrated the detailed luminescence process; Fe acted as a metal-linked ligand and co-reaction accelerator for self-enhanced ECL. The controllable synthesis method for bimetallic sites improved the ECL emission of MOFs, and the synergistic effect between bimetallic ligands enhanced ECL efficiency (Fig. 11b) (Wang et al., 2024 Zhao, Du, Zhang, Li, et al., 2023).

Food analysis applications involving MOF materials have attracted attention for developing physical and smartphone-connected devices that provide useful on-site and reliable data readouts (Tavassoli et al., 2024). Lawati et al. conducted a study where they developed a Co-MOF on luminol-H<sub>2</sub>O<sub>2</sub> on paper to create a chemiluminescence reaction with strong emission and high stability. They also used a smartphone operating system to detect phenolic content in food samples. The hydroxyl radical in phenolic compounds can effectively reduce the luminescence emission of the luminol-H<sub>2</sub>O<sub>2</sub>-CoMOF system. The study found that the

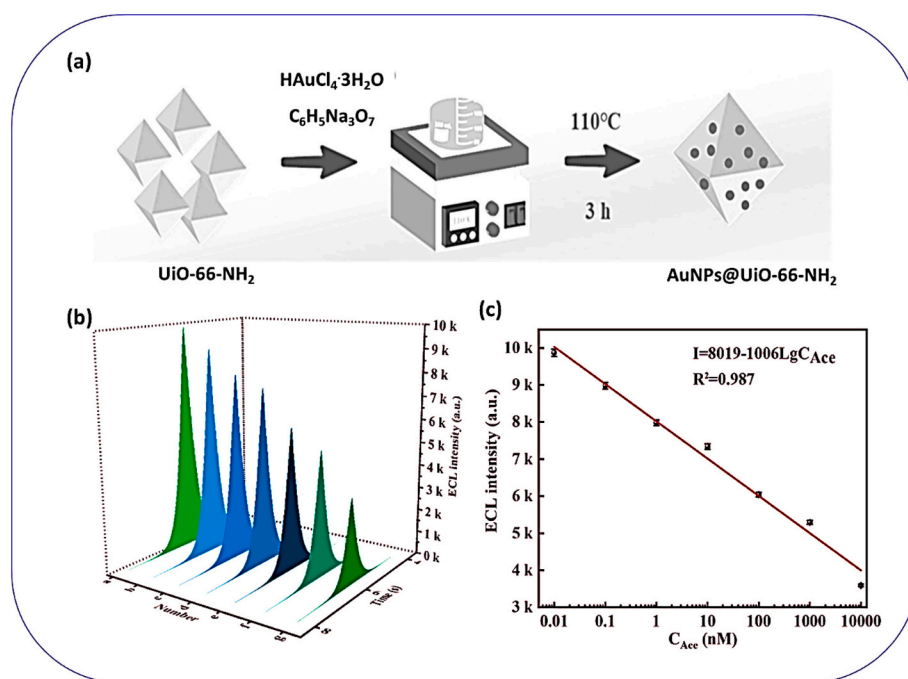
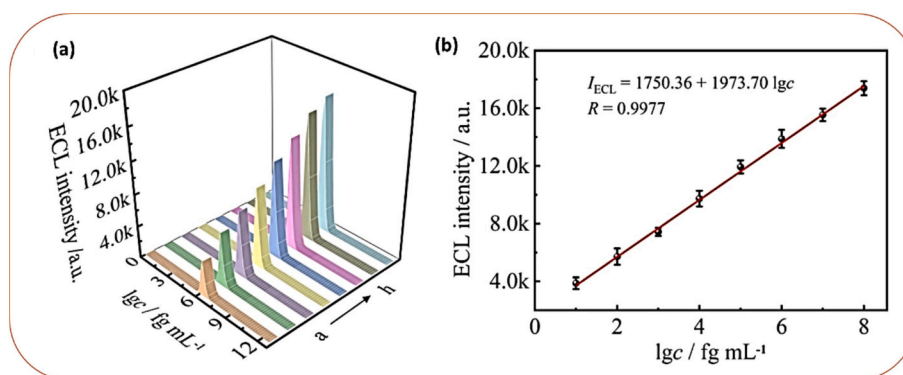
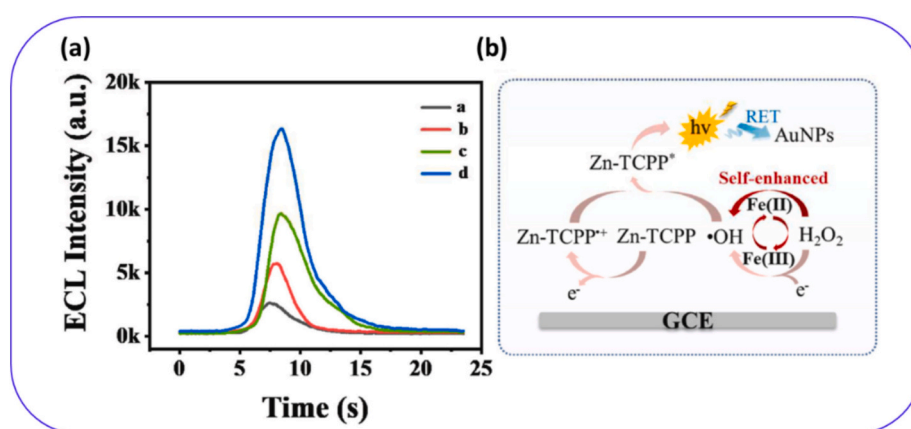


Fig. 9. (a) Schematic presentation of MOF sensor development. (b) The sensor's detection results at 7 ACE concentrations (c) standard curve were obtained by projection on the YOZ plane. Reproduced with the permission of (Li et al., 2025) © 2024 Elsevier B.V. All rights are reserved.



**Fig. 10.** (a) The ECL intensity was observed with the increasing concentration of SDM FROM 0.0 fg/mL to 100 ng/mL (a  $\rightarrow$  h). (b) The observed linear correlations between ECL intensity and the log[C] SDM with error bars representing standard deviation ( $n = 3$ ). Reproduced with the permission of (Liu et al., 2023) © 2023 Elsevier Ltd. All rights reserved.



**Fig. 11.** (a) The ECL curves of (curves a-d) Zn TCPP MOFs, Fe TCPP MOFs, Fe/Zn TCPP MOFs, Fe TCPP(Zn) MOFs in PBS containing 10 mM H<sub>2</sub>O<sub>2</sub>. (b) The mechanism of self-enhanced ECL. Reproduced with the permission of (Wang et al., 2024) © 2024 Elsevier B.V. All rights reserved.

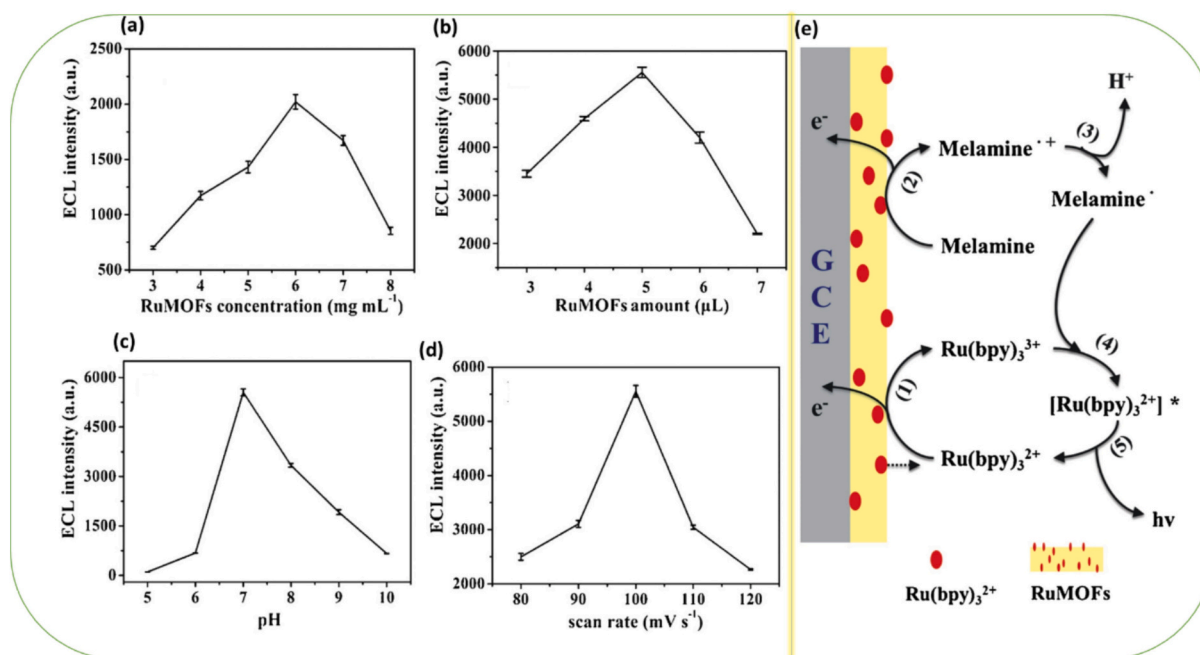
system had low detection limits for gallic acid (0.12  $\mu\text{g/mL}$ ), quercetin (0.28  $\mu\text{g/mL}$ ), catechin (0.46  $\mu\text{g/mL}$ ), kaempferol (0.85  $\mu\text{g/mL}$ ), and caffeic acid (1.23  $\mu\text{g/mL}$ ), demonstrating the practical application of the luminol-H<sub>2</sub>O<sub>2</sub>-CoMOF system with smartphones (Al Lawati et al., 2021). The development of MOF ECL sensors has resulted in significant advancements in achieving a signal-off state. This progress can be attributed to the enhanced performance of the energy donor and acceptor sites within the sensor structure (Cheng et al., 2024). MOFs in ECL for real food sample analysis are effective when combined with co-reactant accelerators, electrocatalytic oxidation-reduction, and label-free sensing (Gloag et al., 2024). The metal sites, clusters, and organic ligands in MOFs can be customized to create luminescent materials. Feng et al. designed tris(2,2'-bipyridyl) dichloro ruthenium(II)hexahydrate ((Ru(bpy)<sub>3</sub>)<sup>2+</sup>) loaded Ru-MOF in which Ru(bpy)<sub>3</sub><sup>2+</sup> were introduced into the MOF for enhancing ECL activity. In single-factor analysis, the fabricated Ru-MOF used to detect melamine in dairy products showed an LOD of  $3.8 \times 10^{-11}$  M in the  $10^{-10}$ – $10^{-4}$  M concentration range. The oxidative-reductive system in Ru-MOFs for the ECL response revealed the redox reactions and oxidation of melamine. The Ru(bpy)<sub>3</sub><sup>2+</sup> to Ru(bpy)<sub>3</sub><sup>3+</sup> played an efficient role in the electron transfer, leading to the ECL intensities and melamine detection process. The practicality applicability of the designed ECL sensor for determining melamine in milk and infant formula powder showed recoveries in 98–104 % and 95–103 %, respectively (Feng et al., 2018). The mechanism demonstrates the electron transfer and ECL emission production by [Ru(bpy)<sub>3</sub><sup>2+</sup>]<sup>\*</sup>. The Ru(bpy)<sub>3</sub><sup>2+</sup>/tri-n-propylamine (TPRA) ECL system first the oxidation of Ru(bpy)<sub>3</sub><sup>2+</sup> to Ru(bpy)<sub>3</sub><sup>3+</sup> and melamine to melamine<sup>•+</sup> with loss of an electron. Then melamine<sup>•+</sup> to melamine<sup>•</sup> with loss of a proton, further

activated melamine<sup>•</sup> and Ru(bpy)<sub>3</sub><sup>3+</sup> to [Ru(bpy)<sub>3</sub><sup>2+</sup>]<sup>\*</sup> responsible for ECL emission (Fig. 12) (Feng et al., 2018).

Using MOFs with MIP film, nanomaterials, and Ru(bpy)<sub>3</sub><sup>2+</sup> has shown remarkable sensitivity in ECL. These components specifically target interactions and enhance the ECL signal when used as oxidative-reductive, hybridization chain reaction, and co-reaction promoters. This discovery is essential because ECL is an extremely sensitive analytical technique for analyzing food samples, ensuring more reliable results for ECL-based assays (Geng et al., 2024; Peng et al., 2024). Undeniable ECL MOF sensors are of great interest in food analysis applications. Table 2 lists the ECL MOF sensors for monitoring food samples and their analytical parameters.

## 5. Challenges & key findings

MOFs have attracted significant attention due to their unique attributes and chemical versatility. ECL sensing of food samples is very effective, but researchers face challenges in materials synthesis, cost-effectiveness, sensitivity, food sample preparation, and real analysis. Additionally, several challenges impact their practical applications. The sensitivity of the ECL signals depends on humidity, temperature, pH, and solvent, which limits the sensor's applications. Bare MOFs are challenging to design as ECL sensors, so they must be fabricated with biomolecules and inorganic and organic materials. In the case of biomolecules such as antibodies, the direction strongly influences fabricated MOFs to develop ECL surfaces. The antibody's direction could affect the analyte's recognition in the solution. Therefore, the material choice for site-specific orientation is critical for developing ECL sensors.



**Fig. 12.** Effects of (a) The concentration effect of Ru-MOFs, (b) Effects of the amount of Ru-MOFs, (c) Effects of pH, and (d) Effects of scan rate on the ECL intensity in scanning range from 0.2 to 1.25 V for melamine concentration of  $1.0 \times 10^{-5}$  M (e) Proposed mechanism for electron and proton transfer in the Ru-MOFs/melamine ECL system. Reproduced with the permission of (Feng et al., 2018) © 2018 Elsevier B.V. All rights reserved.

MOFs' stable interaction with loaded nanoparticles is another challenging task when developing a stable platform. Nanoparticles embedded inside the MOF framework must not alter inherent properties. Stable interactions are necessary to obtain stable and enhanced signals to avoid leakage. Any leakage of immobilized particles can affect sensor performance directly. In addition, modification in frameworks involves blocking agents directly to the electrode surface, and organic functionalities such as thiols, carboxylic acids, amine, etc., can involve nonspecific bindings for real sample analysis.

The role of redox mediators as active species for electron transfer plays a vital role; even with a moderator, good sensitivity, selectivity, and biocompatibility are still challenging. Moreover, poor stability and reversibility limited MOFs applications for their practical applications. Recycling and regeneration for ECL MOFs face difficulties that pose practical applications. The selectivity and capacity in different media still need to be achieved to develop acceptable ECL MOF sensors for food samples. To enhance the stability and reversibility of ECL sensors using MOFs, several strategies can be employed as follows:

- Incorporating specific functional groups into the MOF structure can enhance stability and reversibility. For example, amino groups can improve the sensor's sensitivity and selectivity.
- Surface modification techniques, such as coating the MOF sensor with polymers or thin films, can protect it from environmental factors and improve its performance over time.
- Fine-tuning the synthesis parameters such as temperature, pressure, and solvent composition can lead to MOFs with better stability and reversibility for ECL sensing applications.
- Creating hybrid materials by combining MOFs with other nanomaterials like carbon nanotubes or graphene can provide synergistic effects that enhance sensor performance and durability.

Fabrication costs cannot be ignored when developing ECL sensors; high fabrication costs hinder the MOFs' applications. It is crucial to create cost-effective synthesis methods to make MOFs more accessible for practical applications. ECL MOF food sensor development faces challenges from materials development and needs to solve issues

regarding food sample preparation. Foods have different varieties, and sample preparation is also complicated. Various foods may need different food sample preparation. Food's physical state and biochemical behavior affect MOF-based ECL sensor development. MOFs offer exciting possibilities for food sample analysis, but these challenges are essential to unlocking their full potential in practical applications. Researchers continue to find innovative solutions to solve challenges and limitations with the benefits of MOF food monitoring tools. To reduce the design and fabrication costs of MOFs, several key strategies can be implemented as follows:

- Optimizing the synthesis process by selecting cost-effective precursors and minimizing the use of expensive reagents can significantly lower production expenses. Additionally, scaling up production volume can achieve economies of scale, reducing per-unit costs, especially for high-demand MOFs.
- Exploring alternative fabrication techniques and innovative processes may further enhance cost-effectiveness.
- Using simulated processes and collected data can also help reduce design and fabrication costs. Optimizing synthesis parameters through simulations to minimize waste and energy consumption can lead to more efficient production. Additionally, employing machine learning algorithms to analyze past fabrication data can help predict optimal process parameters, streamline future designs, and contribute to cost savings.

Common methods for scaling up the synthesis of MOFs include base-assisted synthesis, microwave synthesis, flow chemistry, electrochemistry, and dry heating. BASF leads the commercial production of MOFs with its Basolite® brand, which employs electrochemical methods for large-scale manufacturing. Strem produces a variety of MOFs, including CAU-10H, ZIF-8, and UiO-66. In the UK, MOF Technology utilizes mechanochemical extrusion for cost-effective production. Start-ups like NovoMOF and NuMat Technologies offer customizable MOF synthesis solutions, while Framergy focuses on scaling the production of iron- and titanium-based MOFs (Crawford et al., 2017; Czaja et al., 2009). The methods for large-scale MOF production have evolved to include more

**Table 2**  
MOF ECL sensors for food samples analysis and their analytical performances.

| MOFs                      | Composite materials   | analyte  | LODs                                     | Linear range   | Mechanism insights  | Sample source             | Ref.                     |
|---------------------------|---|--|--|--|---|---------------------------|--------------------------|
| ZIF-8                     | MP QDs  | AFB1   | 3.5 fg/mL                                | 11.55 fg/mL to 20 ng/mL  | Surface state passivation triggered electron relaxation or hole injections  | Corn                      | (Wang et al., 2023)      |
| UiO-66-NH <sub>2</sub>    | CdS QDs-aptamer   | AFB1   | 7.8 fg/mL                                | 50 fg/mL to 5 ng/mL  | co-R, Radicals formed, persulfate lost electrons, persulfate anion radicals reacted to produce CdS QDs* and returned to ground state accompanied by light radiation   | Corn                      | (Huang et al., 2024)     |
| Ni-Co-MOFs                | Au@luminol and CdS QDs  | Pb (II) and S.aureus   | $1.9 \times 10^{-3}$ ng/L and 1.3 CFU/mL | $1 \times 10^{-3}$ - $1 \times 10^6$ ng/L and 0–1 $\times 10^7$ CFU/mL | Catalyze the co-R; CdS QDs are reduced to CdS QDs* <sup>−</sup> . Free radicals form an excited state substance, which jumps to the ground state, releasing energy and light as ECL signals   | Scallops and fish         | (Zhai et al., 2024)      |
| Zr-MOF                    | DNA   | Salmonella   | 37 CFU-m/L                               | 50 CFU/mL–5 $\times 10^6$ CFU/mL                                       | HCR; Aptamer switches probe, primer hybridization forms dsDNA. Salmonella release for signal amplification. ECL emitters PCN-224 attached to SH-DNA. Degradation of ssDNA detaches PCN-224, reducing ECL signal   | Milk                      | (Wang et al., 2023)      |
| MOF@Apt2                  | Pb <sup>2+</sup>  | VP   | 1.7 CFU/mL                               | 1 to 10 <sup>8</sup> CFU/mL  | Pb <sup>2+</sup> embed Ru-MOF binds to amino-modified Apt2. Dual-mode aptasensor has thiol-modified Apt1 on gold electrode. Ru-MOF size overlaps on VP. Ru-MOF aids electron exchange between electrode and Pb <sup>2+</sup> .  | Oyster and seafood        | (Wei et al., 2020)       |
| Eu <sup>3+</sup> -MOF-253 | Au-NPs  | carbaryl   | 0.14 µg/L                                | 0.2–200 µg/L   | Catalyze the co-R; electron transfer and generated Eu <sup>3+*</sup> , enhancement in ECL intensity   | Milk and soybean oil      | (Liu et al., 2022)       |
| Tb-MOFs                   | Au-Cu   | CPF  | 0.029 pg/mL                              | 0.1–106 pg/mL  | co-R action promoters, doped Au and Cu acted as core reaction accelerators  | Cabbage & apple           | (Fang et al., 2024)      |
| Cu/Co-MOF                 | g-C <sub>3</sub> N <sub>4</sub> and luminol–H <sub>2</sub> O <sub>2</sub> | acetamiprid and malathion                                    | 0.015 pM, and 0.018 pM                   | 0.1 µM ~ 0.1 pM  | ER; Through cDNA-aptamer recognition, a double helix forms with signal probes. Luminol and g-C <sub>3</sub> N <sub>4</sub> produce ECL signals, and the addition of pesticides causes DNA helix to unravel, probe to fall off, and ECL signal to decrease                                       | Apple and tomato          | (Liu et al., 2021)       |
| Ce-MOF                    | AuNPs and dsDNA   | sulfadimethoxine (SDM)                                       | 1.28 fg/mL                               | 10.0 fg/mL to 100 ng/mL  | DA, co-R; First, ZPM and S <sub>2</sub> O <sub>8</sub> <sup>2−</sup> are reduced to ZPM* <sup>−</sup> and SO <sub>4</sub> <sup>•−</sup> . Second, ZPM* <sup>−</sup> and SO <sub>4</sub> <sup>•−</sup> reactions generate excited states (ZPM*), improving ECL emission.                         | Milk                      | (Liu et al., 2023)       |
| Zn-MOF                    | Ru(bpy) <sub>3</sub> <sup>2+</sup>  | brilliant blue FCF (BB)                                      | $2.5 \times 10^{-8}$ M                   | ≈ 1.0–7.0 µM   | ER; Ru(bpy) <sub>3</sub> <sup>2+</sup> and TEA oxidized to form Ru(bpy) <sub>3</sub> <sup>•+</sup> & TEA* <sup>•+</sup> , respectively. TEA* <sup>•+</sup> converts to TEA*. Ru(bpy) <sub>3</sub> <sup>2+</sup> is reduced by TEA* to Ru(bpy) <sub>3</sub> <sup>•+</sup> , causing ECL emission | Juice                     | (Shan et al., 2019)      |
| Fe TCPPP(Zn) MOFs         | AuNPs-Apt   | KAN  | 0.28 fM                                  | $1.0 \times 10^{-7}$ – $1.0 \times 10^{-13}$ M                         | co-R, ECL-RET; In KAN, aptamers remove AuNPs probes from the electrode surface, inhibiting the RET system. A suppressed RET system enhances ECL signal restoration, allowing KAN detection.   | Milk, honey, & pond water | (Wang et al., 2024)      |
| Co-MOF                    | luminol–H <sub>2</sub> O <sub>2</sub>                                     | gallic acid, quercetin, catechin, kaempferol, & caffeic acid | 0.12, 0.28, 0.46, 0.85, & 1.23 µg/mL     | 0.12–1.23 µg/mL  | ER, CL emission of luminol–H <sub>2</sub> O <sub>2</sub> –Co-MOF  | Honey, molasses & tea     | (Al Lawati et al., 2021) |
| Ru-MOF                    | Ru(bpy) <sub>3</sub> <sup>2+</sup>  | melamine   | $3.8 \times 10^{-11}$ M                  | $10^{-10}$ – $10^{-4}$ M   | Oxidative-reductive involves Ru-MOFs & melamine, producing ECL from redox reactions during melamine oxidation. Luminescence by [Ru(bpy) <sub>3</sub> <sup>2+</sup> ]* as it returns to ground state   | Milk                      | (Feng et al., 2018)      |

AuNPs double-stranded DNA (dsDNA), cadmium sulfide (CdS), quantum dots (QDs), tris(2,2′-bipyridyl) dichlororuthenium(II) hexahydrate (Ru(bpy)<sub>3</sub><sup>2+</sup>), carbon nitride nanosheet (g-C<sub>3</sub>N<sub>4</sub>), double-stranded DNA (dsDNA), methylamine perovskite quantum dots (MP QDs); chlorpyrifos (CPF), *Vibrio parahaemolyticus* (VP), Aflatoxin B<sub>1</sub> (AFB1), kanamycin (KAN), donor-acceptor (DA), co-reactant formation (co-R) electrochemically redox (ER), hybridization chain reaction (HCR)

effective technologies, like mechanochemical synthesis, which help reduce costs. However, commercially available MOF products are often limited to well-known archetypical MOFs due to the availability of organic linkers. It is worthwhile to explore the large-scale production of other promising types of MOFs, such as zirconium-based MOFs. Most MOFs tend to be unstable in water because of the hydrolysis of their bonds. Nevertheless, post-synthetic processes and conversion into

functional carbon materials present new opportunities for commercialization. There are many possibilities for those interested in entering the MOF commercialization market (Paul et al., 2023; Teo et al., 2021).

It has been found that most bare MOF materials are not particularly selective in detecting or recognizing analytes from food samples. Using these materials alone may not be the most effective approach for designing new fabricated MOFs that can accurately sense and identify

specific compounds within food samples (Hendon et al., 2017). Instead, utilizing an array-based device or employing computational screening techniques may be more successful in developing new and improved MOFs. It is worth noting that traditional polymer-based materials used for food sample analysis have also lacked effectiveness. However, combining MOFs with other materials could provide a more suitable sensing platform for detecting and analyzing various compounds within food samples. Despite these challenges, there is a reason for optimism regarding using MOFs as food sensors. Recent experimental and computational screening investigations have yielded promising results, indicating that with further research and development, MOFs could become a valuable tool in food analysis and safety (Zhang, Meng, et al., 2024).

Indeed, some key findings are related to MOFs and their ECL sensing applications for food sample monitoring. MOFs with crystalline structures have been used diversely as ECL sensors. MOFs exhibited strong fluorescence, chemical functionality, and affinity for probes, enabling them to have promising applications for detecting various analytes (Shubhangi et al., 2024). Bare MOFs are less efficient and active in ECL compared to fabricated MOFs. The findings show that encapsulating a ruthenium(II) complex into MOFs enhanced ECL activity. For example, tris(2,2-bipyridyl)dichlororuthenium(II) hexahydrate,  $\text{Ru}(\text{bpy})_3^{2+}$  loaded Zn-MOF with large internal surface areas acted as ECL emitter for dopamine. The MOF loaded with Ru molecules inside and leakage could be prevented, which is responsible for stable and enhanced ECL signals (Li et al., 2018).

MOF ECL sensors use light and conductive properties to detect analytes, and functionalities or composite materials can act as signal-amplifying agents (Chang et al., 2023). It is crucial to use photoactive materials as agents to increase the strength of signals and show various effects on signals, such as the antenna effect (Zhao, Wang, Wang, Fan, et al., 2023). This could be possible only with high-quality materials and advanced manufacturing techniques (Liang et al., 2024). For example, A Ru@MOF with  $\text{Ru}(\text{bpy})_3^{2+}$  ECL is used as a sensing platform for kanamycin A (KANA) designed with an  $\text{Ag}^+$ -dependent DNAzyme. Interestingly, the stem-loop DNA (HP) quenched the ECL emission of MOF with the ferrocene (Fc). The DNAzyme dependence on  $\text{Ag}^+$  for KANA recognition through HP cleavage is released at the Fc end to restore the ECL signal (Zheng et al., 2024). As research emerges into MOF ECL

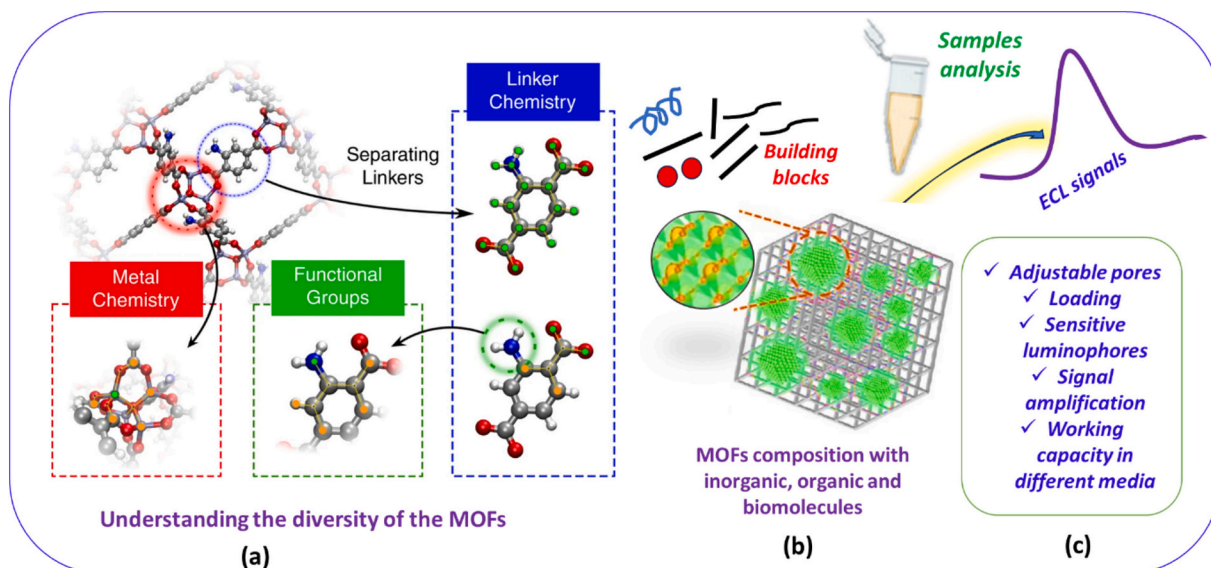
sensors, there is a need to explore new ways to improve their performance and expand their capabilities, which can be tailored to specific applications by adding different chemical groups or functional units. The large surface area of MOFs allowed analytes to interact analytes with signal amplifiers, making them a vital tool for food sample analysis.

Moreover, developing MOF ECL food sensors involving and generating hypothetical structures needs new strategies to fulfill the purpose, which could include combined results of computational and experimental outcomes (Zhiwei Lu et al., 2023; Long Zheng et al., 2023). The structural building blocks of MOFs closely resemble the chemical intuition, a combination of pore geometry and chemistry of metal nodes, ligands, and functional groups. For example, inserting a functional group can sometimes change pore shape, and properties may be interpreted due to the pore-shape effect (Moosavi et al., 2020). To describe the development of nanoporous MOF materials for food analysis, pore geometry, including pore size and volume, must have structure-property relationships with fabricating materials by including all domains within an individual sample, metal-linker chemistry, and functional groups (Fig. 13).

## 6. Conclusion

In conclusion, MOF ECL sensors have shown excellent applications in food sample monitoring, but there is still much attention for improvement. Literature reports are subjected to MOF fabrication using traditional methods for signal generation. However, ECL sensor development has been designed significantly beyond a limited approach due to signal transduction and high-sensitivity advances. Furthermore, ECL MOF sensors have significant applications in real food sample analysis, including grains, fruits, vegetables, meats, and beverages. Various lumiphores and organic and inorganic materials have enhanced MOF ECL sensitivity when developing food sensors.

Besides these advantages, several critical points have been observed during the study. When MOF materials synthesis is limited to only a few signal changes, approaches must apply new techniques to obtain particular structures. Due to suitable interfaces between frameworks and support surfaces, the new methods could help access different MOF structure length scales for ECL sensing applications. More biocompatible and environmentally friendly ECL reagents are highly desirable to fulfill



**Fig. 13.** The combined work of computational and experimental research helps in crystal graph monitoring for improved ECL properties. (a) Understanding MOF diversity with computational studies, linker and functional-group graphs, the start atom (in green), and the nearby atom (in orange). Reproduced with the permission of (Moosavi et al., 2020) Copyright © 2020, The Author(s). (b) Schematic representation of MOF design by compositing with inorganic, organic, and biomolecule materials (c) Proposed high sensitivity of ECL signals and improved properties of MOFs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ECL analysis for the real samples analysis. MOFs-based ECL emitters rely on high positive or negative voltage for ECL reactions. They could also have side effects such as electrical damage to cells, hydrogen/oxygen evolution reaction, electrode passivation, electrical damage of cells, and hydrogen/oxygen evolution reaction. It can't be denied that low-voltage-driven ECL luminophores need to be combined with other electro-generation techniques to generate MOF-based effective sensing platforms. Novel ECL MOF emitters detect weak bioelectricity from various highly sensitive activities for analyzing food samples. ECL MOF sensors provide significant opportunities for contaminant detection and analytical device development. Future ECL MOF research in food safety should focus on:

- Designing new multifunctional ligands and developing MOFs with increased sensitivity for various analytes in food, especially in remote areas.
- Implementing machine learning and high-throughput techniques could lower design costs and time for industrial-scale MOFs. Using different metal ions may produce materials with unique sensing abilities; stability studies in real-world applications are essential.
- Combining MOFs with highly conductive materials will enhance ECL intensity. Conductivity durability studies are crucial for performance under different conditions. Understanding degradation factors over time is vital for reliability.
- ECL MOFs are promising for multi-analyte detection in complex food matrices. Designing MOF-based sensor arrays to detect multiple contaminants simultaneously will improve efficiency and accuracy. Exploring different immobilization strategies to integrate multiple recognition elements in a single MOF is essential for performance.

#### CRediT authorship contribution statement

**Brij Mohan:** Writing – review & editing, Writing – original draft, Formal analysis, Conceptualization. **Stefan Rućman:** Writing – original draft, Formal analysis. **Pisith Singjai:** Writing – review & editing, Formal analysis. **Armando J.L. Pombeiro:** Writing – review & editing, Supervision, Formal analysis. **Wei Sun:** Writing – review & editing, Formal analysis. **Gurjaspreet Singh:** Writing – review & editing, Formal analysis, Conceptualization. **Peng Ren:** Conceptualization, Formal analysis, Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Data availability

No data was used for the research described in the article.

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