Applications of SNW₁ Covalent Organic Framework in Analytical Chemistry: A Brief Outlook

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ABSTRACT

Schiff base network₁ (SNW₁) is a recently synthesized covalent organic framework (COF) that has garnered significant interest in the field of materials science and chemistry. It is synthesized through the condensation reaction of melamine with terephthaldehyde and has abundance of imine functional groups present within its chemical structure. Due to its distinctive characteristics such as elevated specific surface area, exceptional thermal and chemical durability, simple synthesis process, and notable electrochemical conductivity, numerous investigations have been conducted on this COF across diverse analytical chemistry domains. Our research group also explored the applications of this COF and its composites in different fields like microextraction methods, adsorptive removal of environmental contaminants, and electrochemical sensing of heavy metals. In this respect, we decided to introduce SNW₁ COF in this short review and have a detailed discussion on its chemistry, and its scrutinized applications in analytical chemistry. Additionally, the literature that has been analyzed yielded pivotal insights, and a set of suggestions have been formulated for subsequent scholarly pursuits.

Keywords: Covalent organic frameworks, Schiff base network₁ (SNW₁), Electrochemical sensors, Microextraction, Adsorptive removal, Analytical Chemistry.
Introduction

Covalent organic frameworks (COFs) represent a category of porous, crystalline substances distinguished by their distinctive configuration and attributes. These materials are constructed from organic units interconnected through robust covalent linkages, culminating in a supremely organized and resilient lattice. The burgeoning interest in COFs can be credited to their prospective utilities across a multitude of domains, including but not limited to, gas encapsulation, catalytic actions, detection technologies, and optoelectronic applications. A salient merit of COFs lies in their customizable pore sizes and surface features [1]. Through meticulous choice of building blocks and manipulation of reaction conditions, researchers have the ability to intricately regulate the dimensions, morphology, and chemical surroundings encompassed within the COF framework [2]. This level of control allows for the design of COFs with specific properties tailored for a wide range of applications. For example, COFs can be engineered to selectively adsorb certain gas molecules, making them promising materials for gas storage and separation technologies [3]. Beyond their adjustable porosity, COFs demonstrate considerable resistance to thermal and chemical stress, rendering them appropriate for deployment in severe conditions. This stability arises from the strong covalent bonds that hold the framework together, providing excellent structural integrity even at elevated temperatures or in the presence of reactive chemicals [4]. As a result, COFs have the potential to be used as robust catalyst supports for various chemical reactions, where stability and recyclability are critical factors [5]. Furthermore, COFs can be designed to possess unique electronic and optical properties, making them attractive for applications in electronics and photonics [6]. Upon integration of π-conjugated constituents into the scaffold, COFs can manifest semiconducting properties and effective charge conveyance, critical for the functionality of electronic apparatuses, including field-effect transistors and light-emitting diodes [6]. Moreover, the precise arrangement of these building blocks within the COF structure can lead to interesting optical properties, including fluorescence and nonlinear optical responses, opening up possibilities for use in sensors and photonic devices [7]. As research in the field of COFs continues to advance, new synthetic strategies and design principles are being developed to further expand the scope of COF materials. For instance, dynamic COFs that can undergo reversible structural
transformations have been reported, offering opportunities for stimuli-responsive materials and molecular machines. Additionally, efforts to scale up the synthesis of COFs and improve their processability are underway to facilitate their practical applications [8].

One common method for synthesizing COFs is through the condensation of building blocks containing reactive functional groups. These building blocks can be linked together through covalent bonds to form a two-dimensional or three-dimensional framework. The condensation reaction can be carried out under solvothermal conditions, where the building blocks are dissolved in a solvent and heated at elevated temperatures to promote the formation of covalent bonds [9]. Alternatively, the reaction can be carried out under neat conditions, where the building blocks are heated in the absence of solvent. Another method for synthesizing COFs is through the self-assembly of preorganized building blocks. In this approach, the building blocks are designed to have complementary interactions that drive their assembly into a specific COF structure. For while hydrogen bonding interactions can drive the formation of three-dimensional COFs. In addition to these methods, researchers have also developed techniques for synthesizing COFs on solid supports, such as metal-organic frameworks or porous polymers. In an investigation by Mullen and colleagues, a variety of covalent organic frameworks (COFs) were synthesized via the condensation of melamine with distinct configurational isomers of phthalaldehyde [10].

These COFs have been designated as Schiff base networks (SNW), reflecting the preponderance of imine functionalities within their composition. Moreover, a particular COF synthesized through the condensation of melamine with terephthaldehyde was distinguished and has been denoted as Schiff base network1 (SNW1)[11]. The molecular architecture of SNW1 is illustrated in Figure 1. The presence of imine functional groups within these COFs makes them promising candidates for various applications, including but not limited to electrochemical sensing, adsorptive removal of contaminants, fluorimetry, catalysis and optoelectronic devices. Within our research collective, a series of theoretical and empirical analyses have been executed pertaining to the applications of SNW1. The ensuing studies will be succinctly explicated [12].
Applications of SNW₁ in Adsorptive Removal of Environmental Contaminants

COFs offer high chemical and thermal stability for long-term pollutant removal in water treatment and air filtration. Their precise synthesis allows tailored materials optimized for specific contaminant removal, with potential for regeneration and reuse. COFs can effectively remove heavy metals, organic pollutants, and emerging contaminants, offering a sustainable solution for environmental remediation in diverse applications. Ongoing research aims to enhance COFs' adsorption capacity, selectivity, and stability, promising a cleaner and healthier planet.

The research concentrated on evaluating the capability of Schiff base network₁ (SNW₁) to function as an adsorbent for eradicating Methylene Blue (MB), an organic colorant prevalently employed across diverse industrial sectors. The investigation employed density functional theory (DFT) calculations to scrutinize the efficacy of SNW₁ in the adsorption of MB. Geometrical optimization and infrared (IR) frequency computations were performed for the molecular configurations of MB, SNW₁, and their respective complexes, utilizing the computational framework of B3LYP/6-31G (d) for theoretical examination. The results indicated that the interaction between MB and SNW₁ is experimentally feasible, as evidenced by the obtained negative adsorption energies. Additionally, the Gibbs free energy change and adsorption
enthalpy change, both exhibiting negative values, indicated that the adsorption process of MB is exothermic and occurs spontaneously. Moreover, the entropy changes and thermodynamic equilibrium constants, characterized by positive values, suggest that the MB adsorption process is thermodynamically feasible and is accompanied by an increase in disorder throughout the interaction process. In summation, the results underscore the viability of SNW$_1$ as a potent adsorbent for the mitigation of MB, thereby addressing the environmental issues correlated with its extensive utilization in numerous industrial sectors [13].

The creation of this particular COF was realized through an uncomplicated synthetic pathway, followed by a detailed characterization of the COF’s surface employing techniques such as Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and Brunauer–Emmett–Teller (BET) analysis. In the pursuit of refining the experimental protocols, parameters including the COF dosage, agitation period, and the pH level were meticulously optimized. Optimum adsorption was observed at an elevated pH value of 10.0. The gathered experimental data were subsequently subjected to analysis via the Langmuir, Freundlich, and Sips adsorption models, among which the Freundlich isotherm represented the superior correlation. The apex adsorption capacity determined was 65.77 mg of the analyte per gram of the adsorbent material.

The synthesis of this specific COF was accomplished through a straightforward synthetic approach and was followed by extensive surface characterization using techniques such as Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and Brunauer–Emmett–Teller (BET) analysis. Efforts to hone the experimental approaches included rigorous optimization of various parameters, notably the COF quantity, duration of agitation, and pH level. The most effective adsorption was noted at a pH of 10.0. Analytical evaluation of the experimental outcomes was performed using the Langmuir, Freundlich, and Sips isotherm models, with the Freundlich isotherm displaying the most accurate fit. The highest adsorption capability was determined to be 65.77 milligrams of analyte per gram of the adsorbent. [14]

The research delineated herein elaborates on the fabrication and analytical profiling of a magnetic covalent organic framework (M-COF), prepared via an innovative solution-based technique, with emphasis on its application prospects as a magnetic sorbent for colorant
remediation. The constructed M-COF nanoparticles exhibited diameters within the range of 21 to 46 nm, as substantiated by diverse spectroscopic and microscopic methodologies. The MCOF underwent further characterizations pre and post dye sorption employing Fourier-transform infrared spectroscopy (FT-IR) and field-emission scanning electron microscopy (FE-SEM). The proficiency of the MCOF in sequestering Amido Black 10B (AB10B), serving as a representative model anionic dye from liquid media, was explored through magnetic solid-phase extraction methods. This venture principally targeted the refinement of variables instrumental to bolstering the sorption efficiency. The findings signified that the MCOF can efficaciously diminish 20 mg L$^{-1}$ of the dye solution within a remarkable span of 2 minutes. The sorption dynamics were aptly characterized by an adapted Langmuir–Freundlich isotherm, conveying a maximal sorption capacity of 228.07 mg g$^{-1}$, which is ascribed to the extensive surface area of 120 m$^2$ g$^{-1}$. The sorption progression adhered to the Elovich model, evidencing an initial sorption rate of 920.20 mg g$^{-1}$ s$^{-1}$. In addition, the regenerated sorbent showcased an encouraging potential for multiple usage cycles. The chemical interplay of AB10B with MCOF was scrutinized utilizing the quantum theory of atoms in molecules (QTAIM) analytical framework. Collectively, the results advocate that MCOF stands out as an exemplary sorbent for effluent treatment, accredited to its straightforward synthesis, distinguished sorption capacity, brisk sorption kinetics, and the feasibility of sorbent recuperation [15].

**Applications of SNW$^1$ in Microextraction Methods**

Covalent organic frameworks (COFs) have garnered substantial interest in the recent past owing to their distinctive characteristics and promising prospects, particularly in the realm of analytical chemistry's microextraction techniques. COFs' high surface area and porosity enable efficient adsorption and desorption of analytes, and their tailored surface chemistries make them selective for specific compounds. Additionally, COFs exhibit stability, both chemical and thermal, and can be easily synthesized in various forms, making them adaptable to different microextraction techniques. Collectively, these properties make COFs valuable for the preconcentration and extraction of analytes from complex samples, pointing towards their expanding role in innovative microextraction techniques within analytical chemistry.
This study presents an innovative methodology for sampling and evaluating phenolic compounds, specifically phenol, 3-chlorophenol, o-cresol, and p-cresol, in the ambient air using needle traps containing the recently formulated adsorbent, Schiff base network/single-walled carbon nanotube (SNW₁/SWCNT). The synthesis and packaging of SNW₁/SWCNT adsorbent were carried out using a 22-gauge spinal needle. Initially, laboratory conditions were employed to evaluate the effectiveness of this method, followed by its application in real sampling scenarios. In order to create diverse levels of phenolic compound concentrations, a particular temperature was established for a 3-inlet container positioned on a heater. The desorption and breakthrough volume characteristics of the needle trap device filled with SNW₁/SWCNT were evaluated through the implementation of response surface methodology and central composite design techniques. The sensitivity of the method presented was significantly elevated, as indicated by the limit of detection (LOD) and limit of quantitation (LOQ) values which ranged between 0.002-0.011 ng/ml and 0.008-0.037 ng/ml, correspondingly. The utilization of an extraction temperature of 270°C and an extraction duration of 5 minutes resulted in the highest response in peak area. When contrasted with the NIOSH-2546 method, a robust correlation (R² = 0.9812) was identified between the two methodologies. Moreover, the suggested approach demonstrated efficacy in quantifying the levels of specific compounds in the air within a plastic manufacturing facility. Findings revealed that the concentration levels remained under the designated threshold limits for phenolic compounds. This implies that SNW₁/SWCNTs exhibit selectivity, and the proposed technique presents a streamlined single-step process for assessing phenolic compounds in airborne specimens [16].

**Applications of SNW₁ in Electrochemical Sensors**

COFs have shown promise in electrochemical sensing due to their porous and crystalline structure, high conductivity, and tailored pore properties. They can be used to detect environmental pollutants, toxins, and biomarkers, making them versatile for environmental, biomedical, and industrial applications. Additionally, COFs have potential in wearable and portable sensor technologies, offering real-time monitoring in various settings. Overall, COF-based sensors are expected to address current challenges in environmental monitoring, healthcare diagnostics, industrial analysis, and personalized sensing technologies.
A recent in-depth study employed QTAIM computations to analyze the interaction between SNW$_1$ and cations. The findings revealed that SNW$_1$ exhibited a stronger interaction with Hg$^{2+}$ compared to other cations, hinting at its potential as a specific sensor for Hg$^{2+}$ ions. A PVC membrane-coated graphite electrode incorporating SNW$_1$ as a crucial element was created, and after conducting systematic experiments, an optimal membrane composition was determined. The electrode's capability to detect Hg$^{2+}$ was affirmed, showcasing both sensitivity and selectivity. This advancement has promising applications in environmental monitoring and industrial processes, particularly in light of mercury contamination's adverse effects. The use of SNW$_1$ for the electrode highlights the significance of interdisciplinary collaboration and theoretical research [17].

![Calibration Curve]

Scheme 1: Potentiometric determination of Hg (II) by a PVC-membrane ion selective electrode
(Reproduced with permission from reference [17])

The newly developed sensor has demonstrated exceptional precision in detecting Mercury (II) thanks to a Nernstian response slope of 29.8 mV per decade across a wide activity range of 1×10$^{-7}$ M to 5×10$^{-3}$ M. With a remarkable detection limit of 8×10$^{-8}$ M, the sensor exhibits high sensitivity to Mercury (II) ions. The reliability and selectivity of the sensor were confirmed through the matched potential method (MPM) investigation, which verified the absence of significant interferences. Evaluation of the sensor for analyzing Hg (II) in effluent samples, compared with a standard spectrophotometric technique, showcased its accuracy and ability to quantify real-world environmental samples. The schematic representation of the sensor design
(Scheme.1) visually illustrates its key components and operational principles, aiding in comprehension of its structure and functionality. In summary, the sensor displays exceptional sensitivity, precision, and durability, making it a valuable tool for environmental monitoring and analysis.

In a separate investigation, SNW₁ was incorporated onto a glassy carbon electrode via the drop-casting method, enabling the simultaneous anodic stripping square wave voltammetric measurement of Pb²⁺ and Hg²⁺ ions. Extensive characterization of the modified electrode was conducted, employing a range of techniques including Fourier-transform infrared spectroscopy, Scanning electron microscopy, energy dispersive X-ray analysis, cyclic voltammetry, and electrochemical impedance spectroscopy. Subsequently, all crucial experimental factors such as pH, supporting electrolyte type, and instrumental parameters were meticulously optimized to achieve maximum sensitivity. Under these carefully tailored conditions, the developed sensor exhibited a linear response in the concentration ranges of 0.01-0.3 µmol/L for Pb²⁺ and 0.05-0.3 µmol/L for Hg²⁺, with remarkable detection limits of 0.00072 and 0.01211 µmol/L for each respective ion. The optimized experimental conditions included a pH value of 2.0, a deposition time of 150 seconds, an accumulation potential of -1000 mV, a pulse amplitude of 40 mV, a frequency of 50 Hz, and a voltage step of 7 mV. By virtue of these optimized parameters, the designed electrochemical sensor proved to be remarkably effective and successfully enabled the simultaneous detection of Pb²⁺ and Hg²⁺ in various edible samples. The calibration curve for the simultaneous determination Pb²⁺ and Hg²⁺ is shown in Figure 2. This development holds substantial promise for the accurate and efficient detection of these hazardous heavy metal ions in food samples, thereby making a valuable contribution to food safety and public health [18].

In our recent study, we have engineered an electrochemical sensor with the ability to accurately detect low levels of Pb²⁺ ions using square wave anodic stripping voltammetry. The sensor features a glassy carbon electrode that has been modified with an in-situ electroplated bismuth film to enhance sensitivity and selectivity. Additionally, it incorporates a nanocomposite material comprising SNW₁ and Fe₃O₄ nanoparticles enclosed within the SNW₁ matrix to improve sensor performance. These combined enhancements empower the sensor to achieve exceptional sensitivity, selectivity, and detection limits for Pb²⁺ ions. Overall, our newly developed electrochemical sensor represents a significant breakthrough in the domain of heavy metal ion
detection, offering outstanding performance and promising potential applications in environmental and industrial contexts.

![Graph showing calibration curves for lead and mercury ions](image)

**Figure 2:** The achieved calibration curves for the concurrent quantification of lead and mercury ions (Reproduced with permission from reference [18])

The results of the experiment show that when Fe₃O₄@SNW₁ is combined with an in-situ electroplated bismuth film, it significantly enhances the sensitivity of the modified electrode to Pb²⁺ ions. An initial screening of experimental factors using a Plackett-Burman design was followed by optimization through a Box-Behnken design. This method successfully identified and optimized important variables, leading to improved performance of the modified electrode in detecting Pb²⁺ ions. The interaction between Fe₃O₄@SNW₁ and the bismuth film plays a crucial role in this increased sensitivity. The employment of Plackett-Burman and Box-Behnken designs facilitated efficient screening and optimization of influential variables, underscoring the significance of considering the interactions between multiple variables. Under optimal circumstances, the suggested sensor shows a proportional response to Pb²⁺ ions in the range of 0.003-0.3 µmol L⁻¹, boasting an impressive limit of detection (LOD) of 0.95 nmol L⁻¹. The sensor's selectivity towards different ionic species has been thoroughly examined, revealing no significant interferences. Moreover, the functionality of the developed sensor was assessed by
employing it for the quantification of Pb$^{2+}$ ions in 10 distinct edible samples. The achieved recovery percentages varied from 95.56% to 106.64%, underscoring the effective utility of the designed sensor in real-world scenarios whose calibration graph is shown in Figure 3 [19].

In a separate study, we have achieved successful synthesis of a composite material consisting of covalent organic framework embedded with silver nanoparticles (Ag@SNW$_1$) [20]. The synthesis process employed a reduction-based method that was both rapid and straightforward. To comprehensively characterize the synthesized composite, we conducted various analytical techniques including scanning electron microscopy, X-ray diffraction, energy dispersive X-ray spectroscopy, Fourier-transform infrared spectroscopy, cyclic voltammetry, and electrochemical impedance spectroscopy. These analyses provided detailed insights into both the structural and electrochemical features of the composite material.

Subsequently, the synthesized Ag@SNW$_1$ composite was utilized as an electrocatalytic modifier for the highly sensitive and selective measurement of Pb$^{2+}$ and Cd$^{2+}$ cations at extremely low levels using square wave anodic stripping voltammetry. Achieving the highest sensitivity required careful optimization of experimental parameters, and the impact of all significant factors was thoroughly examined. Under the optimized conditions (pH=3.0, deposition time=300 s, deposition potential= -1.3 V), the developed electrochemical sensor exhibited a linear response.
within a wide concentration range of 20-120 nmol L\(^{-1}\) for Pb\(^{2+}\) ions and 30-300 nmol L\(^{-1}\) for Cd\(^{2+}\) ions, with detection limits of 6.9 nmol L\(^{-1}\) and 11.1 nmol L\(^{-1}\), respectively.

Furthermore, we rigorously evaluated the selectivity of the suggested electrode against different ionic species and observed no significant interference, thus demonstrating the excellent selectivity of the fabricated electrochemical sensor. Finally, we successfully applied the electrochemical sensor to determine Pb\(^{2+}\) and Cd\(^{2+}\) ions in different edible samples, highlighting its potential for real-world applications in environmental and food analysis.

In conclusion, the synthesis and characterization of the Ag@COF composite and its successful application as an electrocatalytic surface modifier for the highly sensitive measurement of Pb\(^{2+}\) and Cd\(^{2+}\) cations represent significant advancements in the development of electrochemical sensors for trace metal analysis. The obtained findings of this evaluation hold great promise in addressing the challenges associated with monitoring heavy metal contamination in diverse environmental and food samples, thereby contributing to the advancement of analytical methodologies and ensuring human health as well as environmental sustainability.[19] Scheme 2 shows the steps of electrode modification and calibration diagram for concurrent quantification of Pb (II) and Cd (II).

**Scheme 2:** The steps of electrode modification and calibration diagram for concurrent quantification of lead and cadmium ions

(Reproduced with permission from reference [20])
Conclusion and Future Perspectives

High thermal, and chemical stability, great porosity, good electrocatalytic properties of SNW$_1$ have made it an ideal advanced material in different fields such as electrochemical determination of heavy metals ions including Cd$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, adsorptive removal of methylene blue and amide black 10B, and microextraction of phenolic compounds. The most important point that make this COF different from other routine materials that are employed for the mentioned purposes is the high reproducibility of synthesis procedure, great stability in harsh chemical conditions, and excellent selectivity towards the desired analyte by a simple modification or functionalization step. Therefore, it is recommended that various composites of SNW$_1$ will be synthesized and examined for other analytes. Besides, the applicability of other Schiff base networks COFs like SNW$_2$, SNW$_3$, and SNW$_4$ that are synthesized by the reaction of melamine with biphenyldicarboxaldehyde, isophthalaldehyde, and tris(4-formylphenyl)benzene, respectively, can also been scrutinized. In addition, the development of novel greener approaches (solvent free methods) for the synthesizing of SNW$_1$ is of crucial importance in the studies that are conducted in the future.

References


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