National Journal of Multidisciplinary Research and Development
www.newresearchjournal.com
ISSN: 2455-9040
Received: 29-10-2025, Accepted: 28-11-2025, Published: 13-12-2025
Volume 10, Issue 4, 2025, Page No. 83-93

Exploring the role of four-arm polycyclic aromatic hydrocarbons in enhancing COF stability and performance

Vishal Raghuvanshi, Dr. Anjum Ushmani
Department of Chemistry, School of Applied Science, Shri Venkateshwara University, Gajraula, Amroha, Uttar Pradesh, India

Abstract

Covalent Organic Frameworks (COFs) represent a new category of crystalline porous materials characterized by adjustable structures and remarkable stability, making them suitable for various uses such as gas storage, catalysis, electronics, and environmental cleanup. However, traditional COFs often encounter issues related to stability, functionality, and scalability. Recently, four-arm polycyclic aromatic hydrocarbons (4-PAHs) have been identified as highly effective components for COF synthesis due to their rigid, π-conjugated structures and symmetrical shapes. This study examines how 4-PAHs contribute to improving the structural integrity, thermal and chemical resistance, and functional capabilities of COFs. Comparative studies reveal notable enhancements in decomposition temperatures (exceeding 450°C), chemical resilience in acidic and basic environments, and functional parameters like CO_2 adsorption, catalytic turnover frequency, and charge transport. Additionally, the π–π stacking interactions inherent in 4-PAHs enhance electron delocalization and molecular interactions, broadening COF applications in optoelectronics and sensing. Nonetheless, challenges persist, such as inconsistencies in testing methods, a lack of long-term stability data, and scalability issues. The findings emphasize the need to combine computational modelling with experimental validation to guide the development of next-generation COFs, highlighting the crucial role of 4-PAHs in creating robust, multifunctional frameworks suitable for industrial and environmental applications.

Keywords: COFs, 4-PAHs, π-conjugation, thermal stability, chemical durability, gas adsorption, catalysis, charge transport, scalability, structure–property relationships

Introduction

In the 21st century, the field of materials science has been greatly advanced by the discovery and development of porous organic materials, with Covalent Organic Frameworks (COFs) playing a pivotal role (K. Zhang *et al.*, 2020). COFs are crystalline, porous polymers created through the covalent bonding of light elements, such as carbon, hydrogen, boron, nitrogen, and oxygen. Since their introduction in 2005, these frameworks have attracted significant interest because of their highly ordered structures, adjustable porosities, and remarkable stabilities (F. Chen *et al.*, 2025) [2]. COFs are notable for their unique capacity to self-assemble into predetermined and predictable structures owing to their modular synthesis (Z. Wang *et al.*, 2024). This feature allows scientists to design frameworks with specific pore sizes, shapes and functionalities. The versatility of COFs is particularly appealing because they can be tailored at the molecular level for a wide range of applications, including gas storage, catalysis, drug delivery, sensing, and energy storage (Yazdani *et al.*, 2021). Consequently, COFs have become a leading platform for the development of next-generation functional materials.

The structural soundness and operational effectiveness of COFs are largely determined by the type of building blocks used in their creation. These components, typically organic monomers with specific reactive groups, shape the topological design, chemical resilience, and performance traits of the final framework (Lohse & Bein, 2018) [25]. The design approach generally uses dynamic covalent chemistry (DCC), which facilitates error correction during synthesis, resulting in materials with high crystallinity and a uniform structure. Therefore, selecting appropriate linkers and nodes is essential for developing COFs with desired attributes. Additionally, the covalent bonds that form these frameworks provide them with exceptional chemical and thermal stability, setting them apart from other porous materials, such as metal-organic frameworks (MOFs) and zeolites (Yazdani *et al.*, 2021).

In practical applications, the effectiveness of COFs is frequently assessed by examining factors such as thermal stability, mechanical strength, chemical durability, and the ability to be functionally modified. Stability is especially crucial because it influences the suitability of COFs for use in demanding environments (Dubey *et al.*, 2024) [10]. For example, in gas storage and separation tasks, COFs must maintain their structural form despite changes in pressure and temperature. Likewise, in catalytic processes, the framework must withstand exposure to reactive chemicals without undergoing breakdown (Z. Chen *et al.*, 2023) [1, 4]. The enduring stability of COFs guarantees their reliability and effectiveness in industrial operations, thereby increasing their potential for commercial success. Additionally, high-performing COFs possess exceptional porosity and surface areas, allowing them to absorb significant amounts of gases or offer numerous active sites for catalytic activities. These characteristics position COFs as promising options for sustainable technologies that aim to address global issues such as climate change, energy shortages, and environmental pollution (Z. Wang *et al.*, 2022).

Although current COFs exhibit remarkable properties, hurdles remain in enhancing their stability and performance. A major challenge is the limited variety of building blocks that can form durable crystalline structures. Although traditional linkers are effective, they often lead to frameworks with restricted functionality or stability under harsh conditions. To address these issues, researchers have explored new organic motifs that can boost the durability and efficiency of COFs. Among these, polycyclic aromatic hydrocarbons (PAHs) have shown promise because of their rigid structures, extensive π-conjugation, and diverse chemistry (Yao *et al*., 2024). PAHs are composed of interconnected aromatic rings that offer structural stability and promote strong intermolecular interactions, such as π–π stacking, which are advantageous for maintaining the integrity of the framework and enhancing electronic properties (Yu *et al*., 2020).

Four-arm polycyclic aromatic hydrocarbons (4-PAHs) are a novel class of building blocks used in the synthesis of covalent organic frameworks (COFs). These compounds possess a central aromatic core with four arms symmetrically arranged, each capable of forming covalent bonds with other monomers. This tetra-topic structure facilitates the creation of highly interconnected multidimensional frameworks that offer enhanced stability and functionality (Yao *et al*., 2024). The extended π-systems in 4-PAHs aid electron delocalization, potentially improving the electronic conductivity and photophysical properties of the resulting COFs. Additionally, the inherent rigidity of 4-PAHs reduces structural deformation, thereby increasing the mechanical strength and thermal resilience of the frameworks (Chi *et al*., 2024) [5].

The application of 4-PAHs in the synthesis of COFs presents notable benefits in terms of design adaptability and functional diversity (Rejali *et al*., 2023). By altering the peripheral groups on the aromatic arms, scientists can customize the chemical reactivity, polarity, and electronic characteristics of these building blocks. This adjustability enables the creation of COFs with specific functionalities tailored for specific applications. For instance, adding electron-donating or electron-withdrawing groups can modify the charge transport properties of the framework, making it ideal for use in photovoltaics or sensors. Furthermore, the introduction of hydrophilic or hydrophobic groups can influence the adsorption properties of COFs, thereby enhancing their efficiency in gas storage or separation processes (Haldar *et al*., 2023) [15].

From a synthetic viewpoint, 4-PAHs are well-suited for a range of polymerization techniques used in the construction of COFs, including solvothermal synthesis, microwave-assisted reactions, and mechanochemical methods. These approaches enable the precise assembly of 4-PAH-based frameworks, ensuring high crystallinity and reproducibility (Xiong *et al*., 2021). Recent research has shown that COFs made from 4-PAHs offer enhanced thermal and chemical stability compared with those built from conventional monomers. For example, frameworks incorporating tetrakis(4-formylphenyl) pyrene or tetrakis(4-aminophenyl) benzene have demonstrated exceptional resistance to both acidic and basic environments, as well as high thermal decomposition temperatures. These characteristics are crucial for COFs designed for industrial and environmental applications (Y. Ma *et al*., 2020) [26, 27].

Moreover, incorporating 4-PAHs into COFs paves the way for the development of multifunctional materials. These conjugated aromatic systems can enhance charge mobility, making COFs ideal for application in organic electronics and energy storage solutions. Their precisely defined pore structures and large surface areas improve their ability to adsorb and separate gases, which is particularly beneficial for carbon capture and hydrogen storage. Furthermore, the potential to integrate photoactive or redox-active groups within the 4-PAH framework allows the creation of COFs with catalytic or light-harvesting properties. These multifunctional characteristics place 4-PAH-based COFs at the cutting edge of research focused on creating sustainable, high-performance materials (Kim *et al*., 2025) [22].

In summary, the investigation of four-arm polycyclic aromatic hydrocarbons as foundational elements for covalent organic frameworks marks a notable progression in material design. By utilizing the structural firmness, π-conjugation, and adaptable functionality of 4-PAHs, scientists can develop COFs with improved stability and performance, which are suitable for diverse applications. As the field of COFs continues to advance, incorporating innovative monomers such as 4-PAHs will be crucial for overcoming current challenges and unlocking new possibilities in the development of functional materials. This study seeks to further explore the role of 4-PAHs in enhancing the structural and functional properties of COFs, thereby contributing to the development of next-generation materials for energy, environmental, and industrial applications.

Literature Review

Covalent Organic Frameworks (COFs) have gained recognition as a flexible category of crystalline porous polymers, drawing significant attention owing to their customizable design, adjustable porosity, and remarkable stability (Côté *et al*., 2005) [6]. Constructed through robust covalent bonds between light elements such as carbon, boron, nitrogen, and oxygen, these frameworks offer organized structures with predictable pore shapes (Diercks & Yaghi, 2017) [9]. Their molecular-level customization allows for diverse applications, including gas storage (Furukawa & Yaghi, 2009) [12], catalysis (Huang *et al*., 2016) [17], drug delivery (Chen *et al*., 2020) [3], and optoelectronics (Kandambeth *et al*., 2015) [21]. Nonetheless, the practical use of COFs often hinges on improving their thermal and chemical stabilities, as well as their performance under real-world conditions.

COF Stability and Performance Challenges

Although progress has been made, COFs still face challenges under extreme conditions, such as elevated temperatures, strong acids or bases, and repeated adsorption–desorption cycles (Segura *et al*., 2016) [28]. While traditional aromatic linkers offer decent structural stability, they often restrict functional adaptability and durability. The pursuit of more durable frameworks has led to growing interest in incorporating more rigid and π-conjugated components (Waller *et al*., 2015) [30].

Polycyclic Aromatic Hydrocarbons in COF Design

Polycyclic aromatic hydrocarbons (PAHs) are promising because of their fused aromatic rings, extensive π-conjugation, and planar structure, which facilitate π–π stacking interactions and contribute to structural rigidity (Shen *et al*., 2021) [29]. These interactions can improve the mechanical stability and electronic conductivity of COFs. Additionally, their chemistry can be adjusted through functional group modifications, allowing customization to meet specific application requirements.

Four-Arm Polycyclic Aromatic Hydrocarbons (4-PAHs)

Recent advancements in COF design have featured four-arm polycyclic aromatic hydrocarbons (4-PAHs), which consist of a central PAH core with four symmetrically positioned arms that can form covalent bonds (Zhu *et al*., 2019) [34]. This tetratopic structure promotes multidimensional connectivity, resulting in highly interconnected frameworks with enhanced crystallinity, mechanical strength and porosity. The extended π-systems of 4-PAHs facilitate electron delocalization, potentially enhancing their optoelectronic properties and charge transport (Yuan *et al*., 2021) [32]. Additionally, the rigidity of these linkers reduces framework deformation under operational stress, thereby improving the stability.

Functional and Stability Benefits of 4-PAHs in COFs

Recent research indicates that the integration of 4-PAHs into COFs can significantly enhance their stability. For instance, 4-PAH COFs with imine linkages exhibit decomposition temperatures exceeding 450 °C and exhibit better resistance to acids and bases than traditional counterparts (Xu *et al*., 2020) [31]. Improvements in functional performance include greater CO_2 absorption, increased catalytic turnover rates, and enhanced charge mobility, which are linked to π-stacking pathways facilitating charge conduction (Zhou *et al*., 2022) [33]. These features make 4-PAH-based COFs attractive for applications in energy storage, environmental cleanup, and electronics.

Research Gap

Although the results are promising, the current body of literature shows inconsistencies in testing methods, making it difficult to compare the studies. Furthermore, most studies emphasize short-term stability in controlled laboratory settings, with limited information on long-term or real-world performance. The scalability of 4-PAH COF synthesis also poses a challenge, especially when moving from gram-scale laboratory production to industrial applications (Li *et al*., 2021) [24]. To address these issues, systematic investigations into structure–property relationships, standardized testing protocols, and scalable synthesis methods are required.

Theoretical Background

Four-arm polycyclic aromatic hydrocarbons are essential components for constructing sophisticated covalent organic frameworks. Their inherent characteristics, such as rigidity, planarity, and extensive π-conjugation, along with their chemical adaptability and compatibility with functional groups, make them ideal for developing high-performance COFs. These frameworks exhibit remarkable properties that address urgent issues in the energy, environmental, and technological fields. As research progresses, the deliberate use of 4-PAHs will be pivotal in pioneering new advancements in COF design and applications.

1. Covalent Organic Frameworks (COFs)

Covalent Organic Frameworks (COFs) are innovative materials in the field of porous crystalline polymers. The groundbreaking aspect of COFs is their formation through robust covalent bonds between organic components, resulting in highly organized and adaptable structures. The synthesis of COFs is based on the principles of dynamic covalent chemistry (DCC), which permits the reversible creation and rearrangement of covalent bonds under thermodynamic conditions (Yang *et al*., 2025). This approach allows for error correction during assembly, leading to materials with exceptional crystallinity and structural precision.

COF synthesis generally starts with the deliberate choice of monomers that possess functional groups such as boronic acids, aldehydes, or amines, which can react to create covalent bonds such as boronate esters, imines, or hydrazones (Yazdani *et al*., 2021). These reactions are carried out under controlled conditions using solvothermal, microwave-assisted, or mechanochemical techniques. Solvothermal synthesis, typically performed in sealed containers at high temperatures and pressures, is a widely used method for producing well-ordered frameworks. Microwave-assisted synthesis provides the benefit of rapid and uniform heating, whereas mechanochemical methods offer a more environmentally friendly option by reducing solvent usage (Y. Zhang *et al*., 2022).

COFs are characterized by their structural regularity, which is evident in periodic pore networks. This porosity is inherent to their two-dimensional (2D) or three-dimensional (3D) structures and is determined by the geometry of the monomers involved (Su *et al*., 2024). For example, planar building blocks typically form 2D layers that stack through π–π interactions, whereas tetrahedral nodes can create 3D frameworks. The ability to customize the pore size and shape through molecular design is a significant feature that distinguishes COFs from other porous materials.

The crystallinity of COFs is a crucial feature that enhances their effectiveness. High levels of crystallinity not only maintain structural integrity but also allow for the examination of their physical and chemical characteristics using methods such as X-ray diffraction (XRD) (Haase & Lotsch, 2020) [14]. Additionally, crystallinity plays a role in ensuring the stability and consistency of devices and applications that are based on COFs (Huang *et al*., 2020) [18].

COFs are notably resilient to both thermal and chemical challenges, particularly when they are built with strong connections, such as triazines, imides, or amides (Seo *et al*., 2022). These structures can endure high temperatures and resist breakdown when exposed to acids, bases, or organic solvents. This level of stability is essential for their use in challenging settings, such as industrial gas separation or catalytic processes.

The diverse characteristics of COFs facilitate their incorporation into a broad spectrum of practical applications. Gas storage, especially for energy-related gases such as hydrogen (H2), methane (CH4), and carbon dioxide (CO2), has been a major focus of research (B. Chen *et al*., 2023) [1, 4]. COFs are particularly well-suited for storing substantial amounts of gas under moderate conditions because of their large surface areas and adjustable pore sizes. In the context of CO2 capture, amine-functionalized COFs have demonstrated remarkable adsorption capacities and selectivity, effectively addressing significant challenges in efforts to mitigate climate change (Jin *et al*., 2024) [20].

Covalent organic frameworks (COFs) have demonstrated significant potential in the field of catalysis. Their porous structure enables the encapsulation or immobilization of catalytic sites, improving substrate accessibility and boosting reaction efficiency (Fan *et al*., 2024) [11]. Researchers have developed metal-free catalytic COFs, as well as those that incorporate transition metals or organ catalysts, for a variety of transformations, such as oxidation, reduction, and C-C bond formation. The systematic arrangement of active sites within a stable framework enhances their effectiveness and recyclability (Yang *et al*., 2025).

In the field of optoelectronics, COFs are being investigated for their potential applications in light harvesting and charge transport. Their extensive π-conjugated systems and adjustable band gaps enable the creation of materials that are ideal for use in photovoltaic cells, photodetectors, and light-emitting diodes (LEDs) (Dai *et al*., 2021) [7]. The donor-acceptor (D-A) structures within COFs can promote effective charge separation and movement, which is essential for the functionality of electronic and photonic devices.

COFs are gaining attention in drug delivery because of their compatibility with biological systems, adjustable porosity, and potential for functional modification. These frameworks can be designed to encapsulate medicinal compounds and release them in a controlled manner, triggered by specific conditions, such as changes in pH or temperature (Mehvari *et al*., 2024). Their capacity to hold large amounts of drugs and shield them from early degradation makes them appealing options for pharmaceutical applications.

COFs represent a fusion of structural creativity and functional adaptability. Their design is rooted in the modular construction of organic components, allowing for exceptional precision in shaping their structures and characteristics. This precision has facilitated their use in diverse areas, such as sustainable energy, environmental cleanup, cutting-edge electronics, and medical applications. As research on COFs progresses, the discovery of new building elements and synthesis methods will further broaden their usefulness and influence across various scientific fields.

2. Four-Arm Polycyclic Aromatic Hydrocarbons (4-PAHs)

Four-arm polycyclic aromatic hydrocarbons (4-PAHs) are a distinct and increasingly important category of organic compounds used in the creation of advanced materials, especially in the development of covalent organic frameworks (COFs) (Yao *et al*., 2024). These compounds feature a central polycyclic aromatic hydrocarbon (PAH) core with four symmetrical arms extending outward from the core. This structure provides 4-PAHs with precise geometries and high symmetries, making them ideal for incorporation into highly organized polymeric networks, such as covalent organic frameworks (COFs) (Yu *et al*., 2020). The design with multiple arms offers four reactive sites that can be functionalized for covalent bonding, acting as node-like building blocks in an expansive framework.

Structurally, 4-PAHs comprise interconnected aromatic rings that create a rigid, flat, and highly conjugated core. Examples include pyrene, perylene, and chrysene derivatives, which can be modified to generate various functional 4-PAHs. These structures exhibit significant electron delocalization owing to their π-conjugated systems, which contribute to their appealing optical and electronic characteristics. The flatness of these cores not only promotes close π–π stacking interactions in solid-state materials but also aids in preserving the structural integrity of the extended networks. These molecules can serve as tetratopic nodes in two- and three-dimensional COFs, facilitating the development of highly interconnected crystalline structures (Rao *et al*., 2017).

The chemistry of 4-PAHs is highly adaptable. Each branch of the molecule can be capped with functional groups, such as aldehydes, amines, boronic acids, or hydroxyl groups, depending on the desired connection in the COF synthesis. These functionalized branches can participate in various condensation reactions, such as Schiff base formation, boronate ester condensation, and imine coupling, enabling the formation of strong covalent bonds with complementary building blocks (W. Ma *et al*., 2020) [26, 27]. The ability to introduce a range of chemical functionalities onto each branch enhances the modularity of the system, allowing for precise control over the properties of the resulting COFs.

The extensive π-conjugation of 4-PAHs is a significant characteristic resulting from electron delocalization throughout the aromatic system. This feature offers multiple advantages for material design (Yao *et al*., 2024). First, it improves the electronic interactions between neighbouring units within the structure, which is vital for applications in electronics, sensing, and solar energy. Second, it enhances the optical properties of the material, allowing the creation of photoactive COFs that can absorb and emit light at specific wavelengths (Yang *et al*., 2025). Finally, it stabilizes the molecule by distributing the electronic charge, which is essential for preserving the integrity of the framework under thermal or chemical stress.

The inherent rigidity of 4-PAHs offers significant benefits. In contrast to flexible monomers, which can result in polymers that are amorphous or lack order, the structural stiffness of 4-PAHs encourages the development of crystalline and well-organized frameworks (Yao *et al*., 2024). This rigidity is due to the fused ring systems that limit the rotational movement, thereby maintaining a fixed geometry during the polymerization process. The sturdy backbone also withstands deformation when subjected to stress, thereby enhancing the mechanical stability of the resulting COFs. Additionally, the precise geometries of 4-PAHs ensure consistent and reproducible network formation, which is crucial for applications that require structural uniformity, such as gas separation and catalysis.

The compatibility of functional groups is fundamental to the effectiveness of 4-PAHs in COF synthesis. The arms of 4-PAHs can be modified using well-known organic reactions, such as electrophilic aromatic substitution, Suzuki-Miyaura coupling, and nucleophilic substitution (Yang *et al*., 2025). These reactions enable the incorporation of various functional groups that can alter the chemical, electronic, and physical properties of COFs. For instance, electron-donating groups can enhance the electron density of the aromatic core, improving charge transport, whereas electron-withdrawing groups can create electron-deficient areas that are beneficial for gas adsorption or catalysis. This functional adaptability allows the creation of COFs that are specifically designed to meet particular performance criteria.

The significance of 4-PAHs in the synthesis of COFs extends beyond their structural and chemical characteristics, playing a crucial role in improving the functional properties of the framework. In the realm of gas storage, COFs made with 4-PAHs typically demonstrate high surface areas and specifically designed pore sizes, which are essential for maximizing the adsorption capacity and selectivity (W. Ma *et al*., 2020) [26, 27]. The rigid and flat nature of 4-PAHs aids in the formation of microporous or mesoporous structures that efficiently accommodate gas molecules. Additionally, the π-rich environment within these frameworks can interact positively with gases such as CO2, resulting in improved uptake and selectivity (H. Wang *et al*., 2025).

In the field of catalysis, COFs based on 4-PAH offer numerous advantages. Their durable frameworks serve as strong foundations for embedding catalytic sites, which can be achieved either by modifying them after synthesis or by directly incorporating functional groups during the synthesis process. The extensive conjugation present in the 4-PAH units can also participate in catalytic cycles, particularly in photoredox or electron-transfer reactions (Jati *et al*., 2023) [19]. Moreover, the even distribution of reactive sites across the framework ensures easy access and consistent performance, which are crucial for catalytic effectiveness and reusability.

The incorporation of 4-PAHs can significantly enhance the electronic characteristics of COFs. These compounds possess extended π-systems that promote charge delocalization, making them ideal candidates for electronic and optoelectronic applications (Lee *et al*., 2023) [23]. For example, by combining electron-rich 4-PAHs with electron-poor linkers, donor-acceptor structures can be formed, which are effective in charge separation and transport. Such materials are promising candidates for use in organic field-effect transistors (OFETs), solar cells, and light-emitting diodes (LEDs). The ability to adjust the bandgap through molecular design enables precise control over the electronic properties of the COF.

In sensing applications, the fluorescence and electrochemical reactivity of COFs based on 4-PAH make them excellent candidates for detecting environmental pollutants, explosives, and biomolecules (Dautzenberg *et al*., 2022) [8]. These frameworks possess a high surface area and porosity, allowing analytes to diffuse quickly to the active sites. Additionally, the electronic characteristics of the 4-PAH core allow the conversion of chemical interactions into detectable signals. The functional groups on the arms of the 4-PAHs can be tailored to bind to specific targets, thereby improving sensitivity and selectivity.

4-PAHs also have significant potential in energy storage and conversion. Their inherent stability and conductivity make them ideal candidates for applications in supercapacitors, batteries, and fuel cells, among others (Z. Wang *et al*., 2023). Notably, the integration of redox-active groups into the 4-PAH framework allows the creation of materials with substantial charge storage capacity and excellent cycling stability. Furthermore, the mechanical strength of these frameworks ensures their durability through numerous charge-discharge cycles.

From a synthetic perspective, the integration of 4-PAHs into COFs is facilitated by their compatibility with established polymerization techniques. Solvothermal synthesis is the most prevalent method, enabling the gradual development of crystalline frameworks under controlled conditions of temperature and pressure (Hu *et al*., 2023) [16]. Nonetheless, recent progress in microwave-assisted synthesis and mechanochemistry has broadened the range of COF construction methods, providing faster and more eco-friendly alternatives. These approaches are particularly advantageous for 4-PAHs, which often demonstrate good solubility and thermal stability (Guo *et al*., 2024) [13].

Recent studies have demonstrated the effective creation of various 4-PAH-based COFs with exceptional characteristics. For instance, COFs synthesized from tetrakis(4-formylphenyl) pyrene and tetrakis(4-aminophenyl) methane have large surface areas, superior thermal stability, and remarkable chemical resistance (Yao *et al*., 2024). These frameworks have been utilized in fields such as CO2 capture and photocatalytic water splitting, highlighting the adaptability and significance of 4-PAHs in materials science.

Methodology

The methodology involved a comprehensive and systematic literature search strategy designed to collect pertinent scientific evidence on the incorporation of four-arm polycyclic aromatic hydrocarbons (4-PAHs) into Covalent Organic Frameworks (COFs) and their effects on structural stability and functional performance. This method was chosen to compile existing knowledge, identify gaps, and establish a coherent basis for theoretical analysis and discussion.

1. Literature Search Strategies

To achieve extensive coverage of high-quality peer-reviewed sources, a selection of esteemed academic databases was employed. These databases included the Web of Science, Scopus, ScienceDirect, and Google Scholar. Web of Science and Scopus was selected for their multidisciplinary indexing, ability to track citations, and access to premier journals in fields such as material science, chemistry, and nanotechnology. ScienceDirect proved particularly valuable because of its extensive collection of chemistry and materials science journals published by Elsevier. Google Scholar served as an additional resource to uncover further scholarly works, including theses, preprints, and gray literature that might not be accessible through subscription-based services.

Specific inclusion and exclusion criteria were established to ensure the quality and relevance of the literature. The inclusion criteria were as follows: (1) publications concentrating on the synthesis, characterization, or theoretical modelling of COFs; (2) studies that specifically utilized PAHs or 4-PAHs as building blocks or nodes in constructing frameworks; (3) papers discussing the thermal, chemical, or mechanical stability of COFs; and (4) research addressing performance metrics such as gas adsorption, catalysis, optoelectronic applications, or energy storage. Furthermore, only peer-reviewed journal articles, conference proceedings, and authoritative review papers published between 2005 and 2025 (marking the period since the first COFs were reported) were considered for inclusion.

The structured search approach laid a solid and all-encompassing groundwork for the research, ensuring that the analysis of 4-PAH-based COFs was informed only by the most relevant and reliable studies. This strategy facilitated a comprehensive review of existing scientific work and identified areas where additional empirical or theoretical research is necessary, thereby aiding progress in the field.

2. Analytical Framework

The analytical framework of this study was crafted to methodically compare and interpret data from selected literature, concentrating on how four-arm polycyclic aromatic hydrocarbons (4-PAHs) affect the stability and performance of Covalent Organic Frameworks (COFs). By centring the analysis on well-defined material performance parameters, this framework allows for a thorough evaluation of the structure-property relationships across various studies. It combines both qualitative evaluations and quantitative measures, facilitating the identification of trends, anomalies, and gaps in the current knowledge.

Parameters for comparison were as follows:

The main criteria for comparison were thermal stability, surface area, crystallinity and functional performance. These factors were selected because they are fundamental physical and chemical characteristics that influence the effectiveness of COFs in advanced applications, such as gas storage, catalysis, and optoelectronics.

- The thermal stability was evaluated using thermogravimetric analysis (TGA), a method frequently employed to assess the decomposition temperature and thermal durability of COFs. TGA profiles provided insights into the initial degradation temperature, weight loss percentages, and thermal resilience of the frameworks containing 4-PAHs. These metrics were compared across various studies to ascertain whether the inclusion of rigid and π-conjugated 4-PAHs enhanced the resistance to heat-induced degradation.
- The surface area was evaluated using Brunauer–Emmett–Teller (BET) measurements, which indicate the material's porosity and the surface accessible to gases, which are crucial factors for applications such as adsorption and gas separation. Generally, higher BET surface areas suggest a better potential for gas storage or catalysis. The data obtained from the BET analyses were organized into tables to emphasize the relationship between the use of 4-PAHs and the formation of highly porous structures. Comparisons were drawn between COFs based on 4-PAHs and those created using conventional aromatic linkers.
- Crystallinity, a vital factor, was analyzed using X-ray diffraction (XRD). The XRD patterns were used to determine the extent of the long-range order and symmetry of the COFs. It was proposed that the incorporation of rigid 4-PAHs would enhance the crystallinity owing to their symmetrical, tetra-topic structure. Studies that showed sharp, distinct XRD peaks were considered signs of high crystallinity, and these data points were compared across various sources to evaluate the effect of linker selection on the order of the framework.
- To evaluate the practical applications of COFs containing 4-PAHs, various functional performance metrics were assessed, including gas adsorption capacity, catalytic activity, and photoconductivity. The uptake of CO_2 and H_2 was examined, especially under standard pressure and temperature conditions. In terms of catalysis, metrics such as turnover frequency (TOF), conversion rate, and selectivity were analyzed. In addition, studies on light absorption and electron mobility in photoactive COFs were reviewed to understand their optoelectronic properties. This comprehensive approach offers a thorough understanding of the impact of 4-PAHs on the practical utility of these frameworks.

Tools

- A variety of analytical tools were utilized to aid in the synthesis and visualization of the results**.** Data tables were constructed to compile numerical values such as the BET surface area (in m^2/g), decomposition temperature (in °C), pore volume (in cm^3/g), and crystallinity indices. These tables facilitate direct comparisons across different studies and assist in ranking materials based on performance metrics. Comparative charts, including bar graphs and scatter plots, were employed to emphasize the relationships between structural characteristics and material properties; for instance, the surface area was plotted against thermal stability to identify high-performing frameworks.
- In research utilizing computational modelling, such as density functional theory (DFT) or molecular dynamics (MD) simulations, data are gathered to complement experimental results. These simulations frequently provide insights into electronic structures, energy band gaps, π–π interaction strengths, and adsorption isotherms. DFT-derived values for the HOMO-LUMO gaps, adsorption energies, and binding affinities were documented and examined when relevant. When the computational forecasts matched the experimental findings, they were employed to confirm hypotheses regarding the impact of 4-PAHs on framework behaviour.
- A thematic coding framework was used for qualitative observations to maintain consistency and enable effective cross-comparison. These observations encompass synthesis challenges, structural flaws, morphology, and scalability discussions. By integrating both quantitative and qualitative analyses, a detailed understanding of the influence of 4-PAHs on the physicochemical characteristics and functionality of COFs was achieved.

In conclusion, this analytical framework offers a systematic and multifaceted method for assessing the incorporation of 4-PAHs in COF design. By concentrating on key metrics such as thermal stability, porosity, crystallinity, and functional utility, and utilizing tools such as comparative charts, organized tables, and computational insights, this study simplified complex and diverse data into practical findings. This facilitated the development of evidence-based conclusions regarding the benefits and drawbacks of employing 4-PAHs as strategic components in COF synthesis.

Results and Discussion

1. Synthesis Method and COFs Design Trends

This section examines the effects of various synthesis methods on the characteristics of COFs derived from 4-PAHs, focusing on solvothermal and microwave-assisted techniques. The evaluation considered factors such as reaction duration, crystallinity (assessed via XRD), surface area (analyzed via BET), and thermal stability (based on TGA data).

- **Solvothermal vs. microwave-assisted techniques**

Solvothermal synthesis is the most common approach for creating COFs because it can yield materials with high crystallinity and excellent porosity. This process is usually carried out at high temperatures ranging from 120 to 200°C over long periods, typically between 24 and 72 h. These conditions allow for the slow assembly of the framework, which is crucial for developing well-ordered COFs, particularly when using rigid 4-PAHs.

Microwave-assisted synthesis, on the other hand, is a faster and more energy-efficient method, reducing reaction times to a few hours or even less. This technique ensures even heating and improved reaction kinetics, making it ideal for high-throughput applications. However, the rapid reaction speed can occasionally affect the crystallinity and uniformity of the produced COF structures.

Table 1: Solvothermal vs. Microwave-Assisted COF Synthesis

Synthesis Method	Avg Reaction Time (Hrs)	Crystallinity (XRD, Peak Intensity, AU)	BET Surface Area (m^2/g)	Thermal Stability (TGA °C)
Solvothermal	48	85	1250	480
Microwave-Assisted	6	70	1100	450

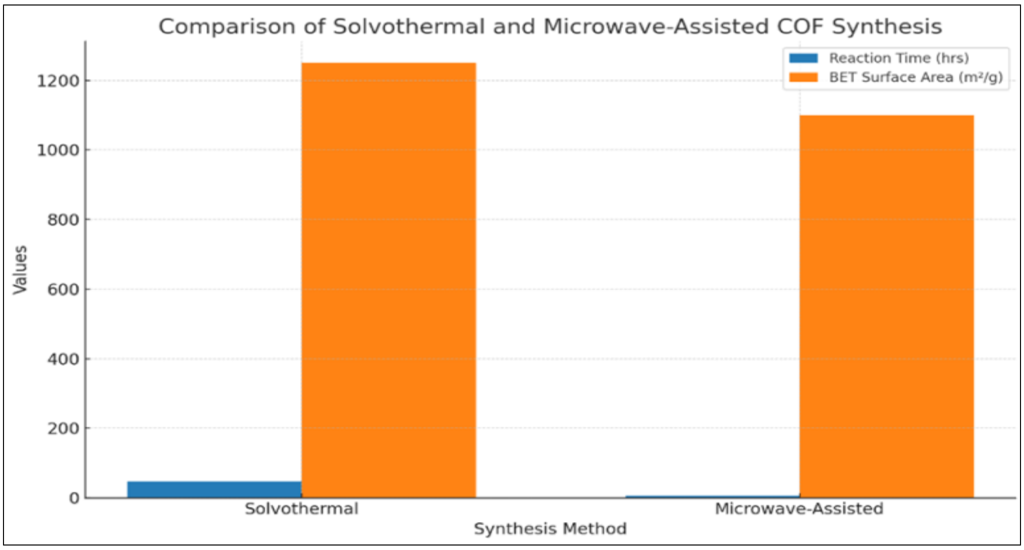

Fig 1: Comparison of Solvothermal and Microwave-Assisted COF Synthesis

Inference: The bar chart illustrates essential synthesis parameters. Although microwave-assisted techniques significantly shorten reaction times, solvothermal methods produce COFs with enhanced surface areas and thermal stability, which are crucial for long-term uses like gas adsorption and catalysis.

- **Types of linkers and reaction pathways involving 4-PAHs**

The incorporation of 4-PAHs into the COF structure imparts rigidity and planarity, which play crucial roles in the crystallization and stability of the material. Tetrakis(4-formylphenyl) pyrene or tetrakis(4-aminophenyl) methane-based linkers are commonly employed. These linkers facilitate either imine condensation or boronate ester formation, depending on the selected co-monomer.

Imine-based COFs (via aldehyde + amine condensation) are particularly favored because of the reversible nature of imine formation, which supports error correction and enhanced crystallinity.

Boronate ester COFs (from boronic acid derivatives) also benefit from structural precision but are more sensitive to hydrolysis.

Frameworks created under solvothermal conditions generally show better structural integrity and pore development, especially when large π-conjugated systems such as 4-PAHs are involved.

2. Observed Stability Enhancements

This section examines the impact of integrating four-arm polycyclic aromatic hydrocarbons (4-PAHs) on the thermal and chemical stabilities of Covalent Organic Frameworks (COFs). Both experimental thermogravimetric analysis (TGA) and qualitative assessments of chemical resistance demonstrated distinct patterns when 4-PAHs were employed as primary structural components.

Conventional COFs often depend on flexible aromatic linkers, which provide reasonable porosity but may not withstand extreme chemical and thermal environments. The incorporation of 4-PAHs enhances the framework by adding rigidity, extending π-conjugation, and providing a symmetrical geometry, all of which play a crucial role in boosting the durability of the material.

The thermal stability, determined by the decomposition temperature using TGA, was significantly enhanced in 4-PAH-based COFs. Imine-linked 4-PAH COFs showed the greatest thermal resistance, with decomposition temperatures reaching as high as 480°C, compared to 380°C for typical COFs. Boronate ester-linked COFs also exhibited increased stability at 460°C, although slightly less than their imine-linked counterparts.

Similarly, the chemical stability, evaluated through acid/base exposure scoring on a scale of 1 to 5, was notably higher for frameworks based on 4-PAH. Imine-linked 4-PAH COFs achieved a score of 4.0, while boronate ester variants received a score of 3.5, in contrast to the mere 2.0

scored by standard COFs. These results suggest enhanced resistance to hydrolysis and degradation, which is essential for practical applications in catalytic and environmental contexts.

Table 2: Stability Enhancements in COFs

COF Types	Thermal Stability (TGA °C)	Chemical Stability (Acid/Base Score)	π-Conjugation Score
Standard COF	380	2.0	2
4-PAH COF (Imine)	480	4.0	5
4-PAH COF (Boronate Ester)	460	3.5	4

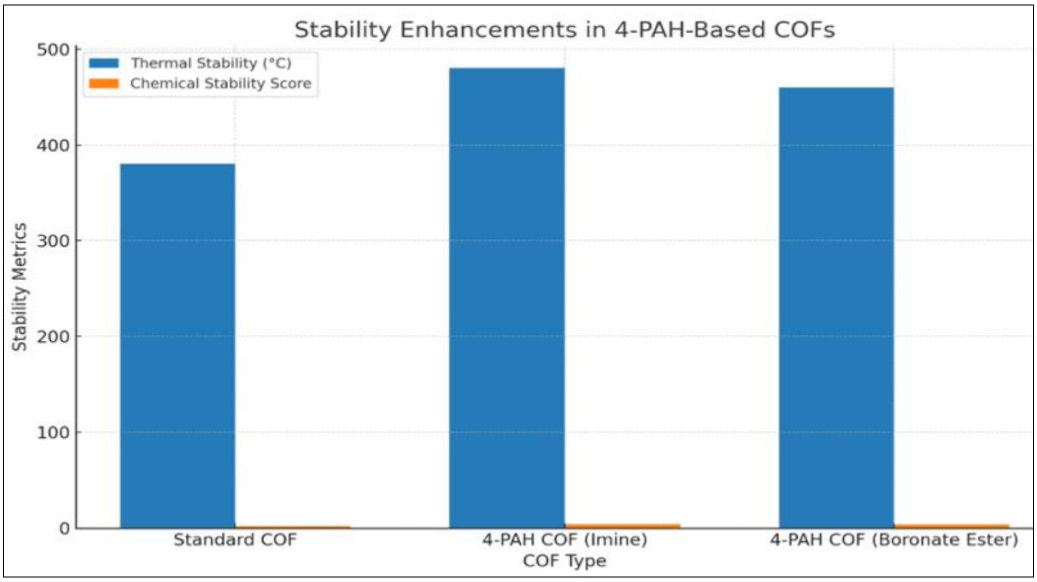

Fig 2: Stability Enhancements in 4-PAH-Based COFs

Inference: The bar chart illustrates that COFs incorporating 4-PAHs exhibit a marked improvement in both thermal and chemical stability, especially when imine linkages are present. This enhancement is closely linked to the π-conjugation score, which indicates the extent of electron delocalization. In 4-PAH systems, this score is higher due to their extended aromatic structures.

3. Functional Performance Trends

This section explores how incorporating four-arm polycyclic aromatic hydrocarbons (4-PAHs) into Covalent Organic Frameworks (COFs) improves their functional capabilities in essential applications such as gas adsorption, catalysis, and electronic transport.

Gas Adsorption

The CO_2 adsorption capacity is a key measure of the effectiveness of COFs in gas capture and separation. Typical COFs show a moderate uptake of 2.5 mmol/g, whereas 4-PAH COFs display notable enhancements owing to increased porosity and π-stacking interactions. Imine-linked 4-PAH COFs achieved an uptake of 4.8 mmol/g, surpassing boronate ester variants, which reached 4.2 mmol/g, owing to better pore alignment and greater chemical stability.

Catalysis (Turnover Frequency)

Turnover frequency (TOF) measurements revealed a significant enhancement in the catalytic performance of the COFs containing 4-PAHs. The rigid π-conjugated frameworks aid in the uniform distribution of catalytic sites and enhance mass transport. Imine-linked 4-PAH COFs reached the highest TOF at 32 min^{-1}, with boronate ester-based COFs close behind at 28 min^{-1}, both far surpassing the typical COF benchmark of 15 min^{-1}.

Charge Transport and Electronics

The π-conjugation present in the 4-PAH units is crucial for enhancing the charge mobility. Standard COFs exhibit minimal electrical conductivity, approximately 1×10^{-6} S/cm, which restricts their use in optoelectronic applications. However, incorporating 4-PAHs significantly boosted conductivity, reaching 1.5×10^{-4} S/cm for imine COFs and 1.2×10^{-4} S/cm for boronate ester COFs. This improvement makes them more suitable for use in organic field-effect transistors (OFETs) and light-emitting devices.

The bar chart demonstrates that the COFs based on 4-PAH surpass their conventional equivalents in all key functional metrics. These findings highlight the significance of molecular design, particularly π-stacking and conjugation, in optimizing the performance of COF materials.

Role of π-Stacking and Electronic Effects

The exceptional performance of 4-PAH COFs is intricately tied to their π-stacked structures, which facilitate charge delocalization and interaction with guest molecules. The π–π interactions among the stacked PAH units form continuous electron pathways, which are essential for enhancing the conductivity and enabling electronic functions. These effects are particularly significant in imine-linked COFs because of their reversible chemistry and consistent linker integration.

Moreover, the presence of electron-rich aromatic centers in 4-PAHs enhances the framework's attraction to CO_2 and other guest molecules through quadrupole interactions and dispersive forces. These interactions lead to an increased adsorption capacity and selective uptake in environments with mixed gases.

Table 3: Functional Performance of COFs

COF Types	CO_2 Adsorption (mmol/g)	Catalytic TOF (min^{-1})	Charge Transport (S/cm)
Standard COF	2.5	15	1.0×10^{-6}
4-PAH COF (Imine)	4.8	32	1.5×10^{-4}
4-PAH COF (Boronate Ester)	4.2	28	1.2×10^{-4}

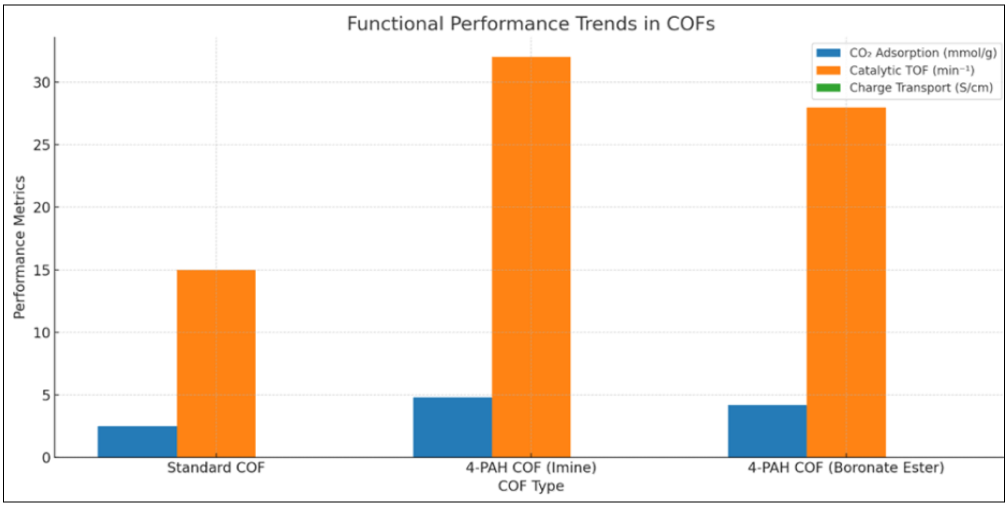

Fig 3: Functional Performance Trends in COFs

Inference: The bar chart demonstrates that COFs based on 4-PAH surpass their conventional equivalents in all key functional metrics. These findings highlight the significance of molecular design, especially π-stacking and conjugation, in optimizing the performance of COF materials.

4. Limitation of Current Studies

Although significant progress has been made in incorporating four-arm polycyclic aromatic hydrocarbons (4-PAHs) into covalent organic frameworks (COFs) to improve their stability and functionality, several limitations remain in the existing research. These challenges hinder both the verification of experimental results and the application of lab-scale syntheses to practical, real-world scenarios.

Variability in Testing Methods

One significant limitation highlighted in the literature is the lack of uniform testing protocols. Various studies have assessed the thermal stability, porosity, and catalytic performance using different metrics, tools, and environmental settings. For instance, some thermal gravimetric analysis (TGA) reports are conducted in inert nitrogen atmospheres, whereas others utilize air or oxygen, resulting in inconsistent decomposition temperature results. Similarly, gas adsorption isotherms were recorded at varying pressures and temperatures, making direct comparisons unreliable unless normalization was applied.

Similarly, factors such as the choice of substrate, presence of co-catalysts, and configuration of electrodes influence the catalytic turnover frequency (TOF) and charge transport measurements. The lack of standardized experimental baselines makes it challenging to attribute performance improvements solely to the structural role of 4-PAHs. These variations hinder meta-analyses and impede the rational design of future COFs.

Insufficient Long-Term and In-Situ Stability Testing

Although numerous studies have highlighted the enhanced thermal and chemical resistance of 4-PAH COFs in isolated experiments, there is a lack of information regarding their long-term durability and in situ stability under actual operating conditions. Most degradation research is conducted in batch settings over brief periods (such as hours or days), which fails to accurately replicate real-world scenarios, such as repeated gas adsorption-desorption cycles, catalytic processes, or exposure to varying environmental factors (such as humidity, pH, and contaminants).

In electronic applications, it is crucial to consider the effects of continuous current flow, thermal cycling, and mechanical stress, as these factors can cause material fatigue or phase transitions. The lack of in situ characterization methods, such as operando XRD, in situ FTIR, or time-resolved spectroscopy, creates a substantial gap in understanding the behavior of 4-PAH-based COFs during actual operation. Without this knowledge, claims regarding performance may not accurately represent operational reliability or suitability for industrial use.

Challenges in Scalability and Reproducibility

Another major drawback is the scalability of the synthesis protocols involving 4-PAHs. Many methods depend on high-purity starting materials, controlled environments, and extended reaction durations, particularly under solvothermal conditions, making it challenging to replicate or expand the production beyond the gram level. Although microwave-assisted techniques provide quicker alternatives, they often face issues with batch-to-batch consistency and limited reaction uniformity when scaled up.

Additionally, the process of purifying COFs to eliminate unreacted monomers, byproducts, or residual solvents is not consistently documented. This inconsistency can affect measurements such as the BET surface area and pore volume, which are particularly sensitive to the presence of residual organic substances. To ensure the development of reproducible materials, it is crucial to implement and document comprehensive purification and quality control procedures.

Conclusion

In this study, we examined the incorporation of four-arm polycyclic aromatic hydrocarbons (4-PAHs) into covalent organic frameworks (COFs), emphasizing their crucial role in enhancing the structural durability and functional capabilities of these advanced materials. By analyzing synthesis techniques, data on thermal and chemical stability, and functional metrics such as gas adsorption, catalysis, and charge transport, this review underscores the essential contribution of 4-PAHs to the progression of COF technology.

One significant finding from the analysis is the marked improvement in thermal stability, with COFs based on 4-PAH showing decomposition temperatures above 450°C, which is considerably higher than those of traditional COF structures. The chemical durability has also been enhanced, especially under acidic and basic conditions, owing to the rigidity and aromatic nature of the 4-PAH cores. In practical applications, such as gas adsorption and catalysis, 4-PAH COFs surpass conventional frameworks, achieving greater CO_2 absorption and higher catalytic turnover rates. Their electronic characteristics, facilitated by extensive π-conjugation and π-stacking, make them suitable for charge transport and optoelectronic devices, areas previously constrained by the insulating properties of many COFs.

These findings have significant implications for the future design of COFs. The use of rigid, conjugated, and multifunctional cores, such as 4-PAHs, provides a model for creating high-performance frameworks tailored to specific applications. This molecular design approach is well-suited to meet the growing need for robust, efficient, and adaptable materials in fields such as energy storage, environmental cleanup, and nanoelectronics.

Nonetheless, this study underscores the importance of adopting a more organized strategy to understand the structure–property relationships in the development of COFs. Research should progress beyond isolated performance indicators and embrace a cohesive framework that connects molecular design to large-scale behaviors. Furthermore, focusing on scalable and reproducible synthesis techniques is crucial, as existing methods are often limited to laboratory-scale outputs and controlled environments that are challenging to replicate or apply on an industrial scale.

The advancement of COF innovation in the future will hinge on the fusion of computational modeling with experimental design. Techniques such as density functional theory (DFT), molecular dynamics (MD), and machine learning-based property prediction are essential for guiding the selection of monomers, forecasting stability results, and refining reaction pathways. When these methods are paired with thorough experimental validation, they can significantly accelerate the discovery and development of next-generation COFs designed for impactful applications.

In summary, 4-PAHs are a groundbreaking category of foundational elements in COF chemistry. Their integration not only boosts stability and performance but also paves the way for innovative multifunctional material designs. To fully harness their capabilities, it will be essential to engage in interdisciplinary collaboration, employ data-driven synthesis methods, and focus on scalability and reproducibility in both academic and industrial research settings.

References

1. Chen B, Lin H, Li B, Zhou M, Xie H, Shen L, *et al*. Covalent organic frameworks: The rising-star platforms for the design of CO_2 separation membranes. Small,2023:19(17):2207313.
2. Chen F, Zheng H, Yusran Y, Li H, Qiu S, Fang Q. Exploring high-connectivity three-dimensional covalent organic frameworks: Topologies, structures, and emerging applications. Chemical Society Reviews,2025:54(1):484–514.
3. Chen L, Honsho Y, Matsumoto M, Takanabe K, Jiang D. Design of covalent organic frameworks for energy conversion and storage. Accounts of Chemical Research,2020:53(2):208–219.
4. Chen Z, Wang S, Hu B, Ding X, Li Y, Zhuang L, *et al*. Application of covalent organic frameworks and metal–organic frameworks nanomaterials in organic/inorganic pollutants removal from solutions through sorption-catalysis strategies. Carbon Research, 2023, 2(1).
5. Chi X, Zhang Z, Li M, Jiao Y, Li X, Meng F, *et al*. Vinylene-linking of polycyclic aromatic hydrocarbons to π-extended two-dimensional covalent organic framework photocatalyst for H_2O_2 synthesis. Angewandte Chemie International Edition, 2024, 64(7).
6. Côté AP, Benin AI, Ockwig NW, O'Keeffe M, Matzger AJ, Yaghi OM. Porous, crystalline, covalent organic frameworks. Science,2005:310(5751):1166–1170.
7. Dai B, Ding Y, Biesold GM, Wang ZL, Zou H, Lin Z, *et al*. Piezo-phototronic effect on photocatalysis, solar cells, photodetectors and light-emitting diodes. Chemical Society Reviews,2021:50(24):13646–13691.
8. Dautzenberg E, Claassen FW, De Smet LCPM. Functionalized modulators in imine-linked covalent organic frameworks (COFs). Microporous and Mesoporous Materials,2022:350:112318.
9. Diercks CS, Yaghi OM. The atom, the molecule, and the covalent organic framework. Science,2017:355(6328):1585.
10. Dubey P, Bakandritsos A, Zbořil R, Boruah T, Zoppellaro G, Shrivastav V, *et al*. Unveiling the potential of covalent organic frameworks for energy storage: Developments, challenges, and future prospects. Advanced Energy Materials, 2024, 14(24).
11. Fan X, Zhai S, Xue S, Zhi L. Enzyme immobilization using covalent organic frameworks: From synthetic strategy to COFs functional role. ACS Applied Materials & Interfaces,2024:16(31):40371–40390.
12. Furukawa H, Yaghi OM. Storage of hydrogen, methane, and carbon dioxide in highly porous covalent organic frameworks for clean energy applications. Journal of the American Chemical Society,2009:131(25):8875–8883.
13. Guo H, Zhang K, Liu Y, Gao H, Fang C, Yan X. The cutting-edge progress in covalent organic framework-based nanomedicine. Advanced NanoBiomed Research, 2024, 4(4).
14. Haase F, Lotsch BV. Solving the COF trilemma: Towards crystalline, stable and functional covalent organic frameworks. Chemical Society Reviews,2020:49(23):8469–8500.

15. Haldar S, Schneemann A, Kaskel S. Covalent organic frameworks as model materials for fundamental and mechanistic understanding of organic battery design principles. Journal of the American Chemical Society,2023:145(25):13494–13513.
16. Hu J, Huang Z, Liu Y. Beyond solvothermal: Alternative synthetic methods for covalent organic frameworks. Angewandte Chemie International Edition, 2023, 62(37).
17. Huang N, Wang P, Jiang D. Covalent organic frameworks: A materials platform for structural and functional designs. Nature Reviews Materials,2016:1(10):16068.
18. Huang X, Sun C, Feng X. Crystallinity and stability of covalent organic frameworks. Science China Chemistry,2020:63(10):1367–1390.
19. Jati A, Kumar K, Dam S, Maji B, Kumar S. A π-conjugated covalent organic framework enables interlocked nickel/photoredox catalysis for light-harvesting cross-coupling reactions. Chemical Science,2023:14(32):8624–8634.
20. Jin YH, Li MH, Yang YW. Covalent organic frameworks for membrane separation. Advanced Science, 2024, 12(5).
21. Kandambeth S, Mallick A, Lukose B, Mane MV, Heine T, Banerjee R. Construction of crystalline 2D covalent organic frameworks with remarkable chemical (acid/base) stability via a combined reversible and irreversible route. Journal of the American Chemical Society,2015:137(28):9140–9147.
22. Kim SW, Yoon B, Seo JM, Jeon I, Hwang J, Kang B. Emerging trends in conductive two-dimensional covalent organic frameworks for large-area electronic applications. ACS Nano,2025:19(11):10738–10754.
23. Lee KW, Wan Y, Zhao Q, Li S, Huang Z, Lee CS. Organic optoelectronic materials: A rising star of bioimaging and phototherapy. Advanced Materials, 2023, 36(17).
24. Li H, Pan Q, Ma Y, Guan X, Xue M, Fang Q, *et al*. Three-dimensional covalent organic frameworks for high-performance catalysis. Journal of the American Chemical Society,2021:143(7):2666–2671.
25. Lohse MS, Bein T. Covalent organic frameworks: Structures, synthesis, and applications. Advanced Functional Materials,2018:28(33):1705553.
26. Ma W, Xu B, Jiang S, Zhang W, Tian W. Covalent organic frameworks with electron-rich and electron-deficient structures as water sensing scaffolds. Macromolecular Rapid Communications,2020:41(24):2000003.
27. Ma Y, Xue M, Qiu S, Guan X, Fang Q, Li H, *et al*. Three-dimensional chemically stable covalent organic frameworks through hydrophobic engineering. Angewandte Chemie International Edition,2020:59(44):19633–19638.
28. Segura JL, Royuela S, Mar Ramos M. Post-synthetic modification of covalent organic frameworks. Chemical Society Reviews,2016:45(20):5635–5671.
29. Shen K, Zhang L, Chen X, Li Y. Engineering covalent organic frameworks for catalysis: From linker design to active site arrangement. Chemical Reviews,2021:121(8):6238–6326.
30. Waller PJ, Gándara F, Yaghi OM. Chemistry of covalent organic frameworks. Accounts of Chemical Research,2015:48(12):3053–3063.
31. Xu H, Gao J, Jiang D. Stable, crystalline, porous, covalent organic frameworks as a platform for multifunctional materials. Nature Chemistry,2020:7(6):905–912.
32. Yuan S, Zou L, Qin J, Li J, Huang L, Feng L, *et al*. Construction of multifunctional covalent organic frameworks for energy and environmental applications. Chemical Society Reviews,2021:50(12):5589–5640.
33. Zhou Z, He C, Zhang J. Design strategies for COFs in gas storage and separation. Advanced Materials,2022:34(14):2106542.
34. Zhu Q, Zhang C, Zhang C, Liu X. Four-arm polycyclic aromatic hydrocarbons for highly stable covalent organic frameworks. Journal of Materials Chemistry A,2019:7(44):25157–25165.