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Covalent Organic Frameworks: Synthesis, Design Strategies, and Diverse Applications

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Abstract: Covalent organic frameworks (COFs) represent an innovative family of crystalline porous polymers that are deliberately designed by employing organic units connected by reversible covalent bonds. These unique features together with permanently porous structure, exceptionally large specific surface area, low density, tunable environment of pores, and outstanding thermal/chemical stability make COFs attractive candidates for novel technologies. In this review, recent progress is presented in the area of design concepts, synthesis methods, structural control, functionalization approaches, and characterization tools of COFs with special consideration to the role of framework topology in the functionality of the resulting materials. Also, growing applications of COFs in the fields of gas storage and separation, heterogeneous catalysis, energy conversion and storage, environmental remediation, chemical sensing, and drug delivery are discussed. The current issues, such as scalable and economically efficient synthesis, hydrolytic stability, processability, and commercialization problems, are described. Lastly, the review covers new trends in COF design, computational material design, hybrid frameworks, and bioapplications, giving perspectives for further research and development.

1. Introduction

Covalent organic frameworks (COFs) are a class of crystalline reticular materials that are unlike any other class of materials because they are composed of light-weight organic building blocks that are held together by strong covalent bonds (Zhu *et al*., 2022; Bukhari *et al*., 2023). They have several unique properties, which distinguish them from traditional porous materials: they feature large surface areas, permanent porosity and atomically precise structural tunability (Luo *et al*., 2021). The modular synthesis approach enables control over pore size, pore geometry, and surface functionality, allowing researchers unprecedented opportunities for rational material design. As COFs are composed of organic components only, they exhibit excellent chemical stability and are endowed with intrinsic biocompatibility in contrast with metal-organic frameworks (MOFs), which rely on metal centers (Chandran *et al*., 2023; Zhu *et al*., 2017; Preethi *et al*., 2025; Chaouiki *et al*., 2026).

Since the first concept was introduced by Yaghi *et al.* in 2005, COFs have evolved from simple examples into very well-designed materials. The field has evolved rapidly and exponentially in terms of structural models and their wide usage (Diercks and Yaghi, 2017; Gropp *et al*., 2020). The early-generation COFs were mainly developed to show the feasibility of covalent construction, whereas

recent studies have highlighted the importance of designing them carefully to meet specific functional demands in more advanced applications such as catalysis and biomedical delivery (Deng *et al*., 2020; Neumann *et al*., 2024; Machado *et al*., 2021).

COFs have several major advantages over conventional porous materials. They have a fully organic backbone, it is bio compatible and does not contain metal toxins that would be of concern in biomedical applications (Marcel *et al*., 2026). The tunable porosity and modular concept enables unprecedented control of the pore attributes and incorporation of functional groups (Esrafili *et al*., 2021). In addition, COFs often have better chemical stability in extreme conditions than MOFs, making them suitable for applications in harsh environments such as acidic or oxidizing media where other materials would be destroyed. Their lightness and large surface area is ideal for use when both required functional efficiency and maximum adsorbent capacity are needed (Liang *et al*., 2023; Shi *et al*., 2023; Li *et al*., 2024; Younas *et al*., 2024)

The COFs are basically divided into two types, two-dimensional (2D) and three-dimensional (3D) frameworks. 2D COFs are the planar extended sheets that are stacked together via weak intermolecular interactions whereas 3D COFs are fully interconnected 3D structures. The topology of COF structures is determined by the geometry of organic linkers and the connectivity of building blocks, enabling a wide variety of topological structures such as hexagonal, kagomé, diamond-like and more complicated high-connectivity architectures. This structural diversity allows systematic optimization of materials for specific applications by rational reticular design principles (Ghosh and Banerjee, 2023; Chedid and Yassin, 2018; Zhu *et al*., 2022).

2. Methodology

This literature review was carried out by conducting a comprehensive study of the scientific literature in order to critically appraise the latest developments in the field of design, synthesis, characterization, functionalization, and applications of covalent organic frameworks (COFs). Scientific articles published in reputable journals from the most important online databases like Web of Science, Scopus, ScienceDirect, SpringerLink, Wiley Online Library, PubMed, and Google Scholar were collected, with an emphasis mainly on works done between 2017 and 2026, although seminal research work carried out before the period mentioned was also taken into consideration for historical purposes. Searches in the databases were performed through the use of keyword combinations like covalent organic frameworks, COFs, reticular chemistry, dynamic covalent chemistry, porous crystalline polymers, COF synthesis, COF characterization, gas storage, energy storage, catalysis, environmental remediation, drug delivery, and biosensing. All the articles selected were written in English and reviewed by peers and contained substantial experimental or theoretical contribution. Only works published in scientific journals and presenting original research results were considered, and duplicates, conference abstracts, and non-scientific works were discarded (Kabir and Lawan, 2024; Kabir *et al*., 2025).

3. History and Development of Covalent Organic Framework

Table 1 shows how covalent organic frameworks (COFs) have developed from the beginning in 2005 to the present as functional materials. It started with the pioneering synthesis of COF-1 and COF-5, demonstrating the possibility of fabricating highly ordered porous frameworks with covalent bonding. Later studies were dedicated to enhancing the structural design, such as designing 2D and 3D COFs with improved crystallinity, porosity, and stability to expand the scope of potential applications (Shahzad *et al*., 2024; Kaur *et al*., 2025). The development of linkage chemistry, monomer design, and

post-synthetic functionalization over the next four years (2017–2020) also propelled the catalytic, electronic, and adsorption-active properties of COFs to new levels, enhancing their performance in energy storage, heterogeneous catalysis, gas separation, sensing, and biomedicine. In recent years, research has also focused on sustainable and scalable manufacturing methods such as 'green synthetic' methods, ‘rapid synthesis’ methods, and ‘framework engineering' using a multifunctional framework, along with computational tools and artificial intelligence for rational material design. The advancement of COFs from a basic laboratory material to potential industrial and environmental application materials, as well as biomedical materials, is reflected in these developments, enhancing the potential of COFs to solve global challenges in clean energy, environmental protection, and advanced functional materials (Shahzad *et al*., 2024; Kaur *et al*., 2025; Tan *et al*., 2023; Dubey *et al*., 2024).

Table 1: Milestones in the Development of Covalent Organic Frameworks

Year	Milestone	Significance
2005	First COFs (COF-1 and COF-5) reported	Introduced the COF family
2007-2012	Development of 2D COFs	Improved crystallinity and porosity
2013-2016	Emergence of 3D COFs	Expanded structural diversity
2017-2020	Functionalized COFs	Enhanced catalytic and sensing properties
2021-present	Green synthesis and multifunctional COFs	Focus on sustainability and industrial applications

Many MOFs have been widely studied due to their outstanding surface area, tunable pore size, and remarkable chemical versatility. Examples are MOF-5, which consists of zinc ions and terephthalic acid; HKUST-1 (Cu-BTC), composed of copper ions and benzene-1,3,5-tricarboxylate; ZIF-8 and ZIF-67, based on zinc and cobalt ions, respectively, linked by 2-methylimidazole; and the zirconium-based UiO-66 and UiO-67, known for their excellent thermal and chemical stability (Cai *et al*., 2021; Yuan *et al*., 2018).

Other examples of interest include the MIL (Materials of Institut Lavoisier) series, such as MIL-53, MIL-100, and MIL-101, which are synthesized using metal centers coordinated with carboxylate ligands, including aluminum, iron, or chromium. Other advanced MOFs, such as PCN-222 (MOF-545), which consists of zirconium clusters and porphyrin ligands, or NU-1000, a zirconium-based framework with pyrene-derived organic linkers, have also garnered significant attention for their excellent catalytic and photocatalytic properties. Due to their unique structural characteristics, these MOFs have been extensively applied in gas storage and separation, catalysis, drug delivery, chemical sensing, water purification, and environmental remediation (Zhang *et al*., 2025; Du *et al*., 2021; Laeim *et al*., 2025)

3. Synthesis Strategies and Methods

3.1 Solvothermal synthesis and the limitations

Until now, COF synthesis has been predominantly carried out by solvothermal methods, where organic monomers are heated in organic solvents at high temperature and pressure for long periods (24-72 hours or more). These traditional methods have been successful in developing basic COF chemistry and creating highly crystalline frameworks with very well-defined porosity (Geng *et al*., 2020; Li *et*

al., 2020). It has important limitations for practical commercialization, since it requires high temperatures and pressures, special equipment, large amounts of toxic organic solvents, and extensive reaction optimization; thus, this method cannot be applied on a commercial scale. Furthermore, the resulting COF powders are insoluble, and thus not processable, which restricts their use in film technologies and membranes. This has led to a high demand for the development of alternative synthetic routes that are environmentally friendly, economical and large-scale (Wu et al., 2025; Kumar *et al*., 2021; Preethi *et al*., 2025; Shahzad *et al*., 2024).

3.2 Room-Temperature and Green Synthesis Approaches

Recent advances have shown that COFs can be formed in aqueous solution at room temperature, which breaks away from the traditional approach of hot synthesis. Ambient aqueous synthesis is based on a careful control of reaction kinetics: preactivation of the aldehyde monomers with acetic acid leads to a strong increase in reactivity in aqueous media (Dai *et al*., 2021; Balasooriya *et al*., 2027). A lower rate of imine formation and higher rates of imine breakdown in water, relative to organic solvents, enable reaction equilibrium to be effectively modulated, allowing highly crystalline products with large surface areas to be crystallized in mere minutes. This approach is shown to be versatile for a variety of monomer families with different size, geometry, pendant groups, and core structures and uses only grams of solvent. Other innovations in COF syntheses on the surface of water (on-water), between two liquids (liquid-liquid), or between two solids (solid-liquid) have also arisen and have their own strengths in controlling crystal growth and resulting thin film and nanopaper processability (Nadaroglu *et al*., 2017; Wu *et al*., 2025; Ariga, 2022).

3.3 Mechanochemical Synthesis

The mechanochemical synthesis has become an especially appealing alternative for COF construction due to its ability to proceed rapidly, without the need of specialized equipment and at room temperature, in air without the use of solvents. Mechanochemistry is a mechanosensitively induced chemical reaction that is conducted in solid or near-solid state without the use of bulk solvents by mechanical energy application such as ball milling (Afshariazar and Morsali, 2022; Marrett *et al*., 2025). The synthesis time can be reduced by 36-100 times, and the solvent consumption by 8-100 times, resulting in a remarkable improvement efficiency. Interestingly, COFs synthesized by mechanochemistry have photocatalytic activity similar to that of solvothermal COFs (Krusenbaum *et al*., 2022). Recent developments have seen the synthesis of boroxine-linked COFs using trimethylboroxine as an assisting reagent in mechanochemical synthesis, and in one-pot Povarov cascades for the synthesis of quinoline-linked COFs, yielding eleven structurally distinct COFs with high crystallinity in about 3.5 hours. The ability to scale up to multi-gram scale (up to 10 grams demonstrated) together with real-time kinetic analysis by Raman spectroscopy can be used to gain insight into the mechanistic pathways (Pan *et al*., 2026; Marrett *et al*., 2025; Afshariazar and Morsali, 2022; Chatzigiannis *et al*., 2025).

3.4 Alternative Methods and Scalability

In addition to solvothermal and aqueous and mechanochemical methods, new ones are constantly being developed to further expand the COF synthesis toolbox. Electrosynthesis allows a COF framework to be assembled by electrochemical reduction, and sonochemical synthesis utilizes ultrasound-assisted reactions to achieve rapid framework formation (Wu *et al*., 2025). Photochemical synthesis is carried out using light energy to activate the monomers, and high-energy ionizing radiation can initiate polymerization reactions. Single-solution phase synthesis reduces the complexity of reaction set-up

because all of the chemistry is carried out under homogeneous conditions and makes chemistry more accessible to researchers that may not have a well-equipped infrastructure. These varied processes all allow the synthesis of COFs under a wide range of reaction conditions from extreme (cryogenic or high-temperature) to ambient, and control of the product morphology from nanoparticles to thin films and bulk crystals. Continuous flow synthesis is another pivotal area that will facilitate the industrial scalability of COFs production for increased reproducibility, as opposed to batch processes. The synthesis of COFs with high crystallinity, porosity and functional group integrity on a scalable level is key to the rapid transition to the clinic and industry (Rodrigues *et al*., 2021; Hao *et al*., 2025)

Table 2: Comparison of COF Synthesis Methods

Method	Advantage	Limitations	Typical Reaction Time
Solvothermal	High crystallinity	Long reaction time	2–7 days
Microwave-assisted	Rapid synthesis	Specialized equipment	Minutes–Hours
Mechanochemical	Solvent free	Lower crystallinity	Minutes
Sonochemical	Fast reaction	Difficult scale-up	Minutes
Room-temperature	Energy sufficient	Sometimes lower crystallinity	Hours
Interfacial	Thin-film fabrication	Limited yield	Hours

Table 2 highlights the major synthetic routes used for the preparation of covalent organic frameworks (COFs), highlighting their pros, cons, and typical reaction times. Though it takes a long time to react (2–7 days) and consumes a lot of energy, the solvothermal method still continues to be widely used since it generates highly crystalline and porous COFs with good structural order. Microwave synthesis, on the contrary, involves the use of special equipment and reduces reaction times from days to minutes or hours by offering fast and homogeneous heating. While lower crystallinity COFs can be obtained via mechanochemical synthesis, this method is a green approach with fewer chemicals and reaction time. Likewise, the ultrasonic irradiation also makes the framework formation faster by sonochemical synthesis but is difficult to be applied to large-scale production. The energy requirement is reduced and processing is simplified by room-temperature synthesis, but the quality of the crystals is not necessarily good. However, the relatively low yield is suitable for the interfacial synthesis of thin COF films for membrane, sensor, and electronic applications. In general, each method has its own set of compromises and advantages in terms of efficiency, crystallinity, scalability, sustainability, and application-specific performance (Wu *et al*., 2025; Desai *et al*., 2024).

4. Structure Design and Single-Crystal Growth

4.1 Reticular Chemistry and Topology Control

Reticular chemistry is the theoretical and practical foundation that enables the prediction and rational design of covalent organic frameworks (COFs), demonstrating that crystal structures can be systematically designed from established principles of molecular geometry, connectivity, and topology (Xu *et al*., 2020; Jiang *et al*., 2021). This approach treats organic linkers as rigid geometric building units and connecting nodes as rigid entities with defined bond angles and coordination environments, allowing predictable assembly into crystalline porous networks (Jiang *et al*., 2021; Freund *et al*., 2021).

By selecting building blocks with specific geometries (linear, trigonal, tetrahedral, etc.), researchers can construct frameworks with predetermined topologies and pore architectures (Xu *et al*., 2020; Zhang *et al*., 2024). Recent advances have demonstrated the synthesis of COFs with unprecedented topological complexity, including 12-connected three-dimensional frameworks and novel topological nets, as well as interlaced unsaturated two-dimensional and saturated three-dimensional architectures (Zhang *et al*., 2024; Cheng *et al*., 2025). By precisely tuning the angular relationships of the constituent building units, the dimensionality of COFs can be controlled through molecular design, enabling the rational synthesis of one-, two-, and three-dimensional frameworks with tailored pore environments and physicochemical properties (Jiang *et al*., 2021; Freund *et al*., 2021). This reticular design strategy has led to the emergence of new COF topologies, including kgd-v and other complex network structures, thereby expanding the structural diversity and application potential of COFs in adsorption, catalysis, sensing, and energy storage (Cheng *et al*., 2025; Zhang *et al*., 2024).

Table 3: Comparison of COFs with Other Porous Materials

Property	COFs	MOFs	Zeolites	Porous Polymers
Composition	Organic	Metal–Organic	Inorganic	Organic
Crystallinity	High	High	High	Usually low
Surface Area	Very high	Very high	Moderate	High
Tunability	Excellent		Limited	Moderate
Thermal Stability	Hogh	Excellent	Very high	Moderate
Chemical Stability	High	Moderate high	Very high	Moderate

Table 3 shows the structural and physicochemical properties of covalent organic frameworks (COFs) relative to other important classes of porous materials such as metal–organic frameworks (MOFs), zeolites, and porous polymers (Machado *et al*., 2022). COFs stand out from other porous materials for their all-organic nature, high crystallinity, exceptionally high surface area, and excellent tunability of the framework structure, which allows for rational molecular design to control pore size, functionality, and framework structure. MOFs have similarly high crystallinity and surface area but also contain the metal ions or clusters, which can often offer increased thermal stability and catalytic activity but may have lower chemical stability under harsh conditions. Zeolites are inorganic crystalline aluminosilicates that are chemically and thermally very stable but have a limited tunability of their structure because of the rigid framework compositions. By contrast, porous polymers are made of organic monomers and tend to have higher surface areas and lower crystallinity and stability due to the amorphous nature of the polymers. The unique properties of COFs, namely their high porosity, crystallinity, lightweight composition, and remarkable design flexibility, render them particularly attractive as catalysts for gas storage, energy conversion, separation technologies, and environmental remediation (Mohamed *et al*., Heravifard *et al*., 2022; Xue *et al*., 2022).

4.2 Single-Crystal COF Synthesis

Single crystal covalent organic frameworks (scCOFs) are a key development in the science of COFs, since the long-range order and structural uniformity of single crystals allows precise characterization of a structure and direct correlation between properties and atomic-level structure. Synthesis of scCOFs is very sensitive to the balancing of nucleation and crystal growth rates to avoid the formation of polycrystalline powder (Liu *et al*., 2024). There are 6 main strategies for scCOF synthesis: (1) modulator-controlled growth, which involves additives to selectively block certain crystal faces and direct growth to desired directions; (2) template- or additive-guided crystallization, which utilizes organic or inorganic templates to guide the assembly of monomers; (3) interfacial synthesis, which exploits liquid-liquid or liquid-solid interfaces to create two-dimensional confined growth spaces; (4) linker-directed design, which introduces specific functional groups that promote the formation of single crystals; (5) rapid crystallization, where nucleation events are minimized by inducing extremely fast growth; and (6) post-synthetic transformation, which transforms polycrystalline COFs into single crystals by controlled transformations. The single-crystal-to-single-crystal transformations realized throughout post-synthetic modification processes provide invaluable mechanistic insights into transformation pathways and enable optimization of structure-property relationships at the atomic scale (Peng *et al*., 2025; Zeng *et al*., 2026; Jin *et al*., 2020).

4.3 Advanced Building Block Engineering

By strategically modifying the structure of organic building blocks, a variety of functional groups and the electronic properties of the COF structure can be incorporated. Twisting building blocks from planar to tetrahedral structures opens up additional possibilities beyond the standard designs for systematic modulation of framework structure and dimensionality (Geng et al., 2020; Qian and Jiang, 2024). The incorporation of electroactive components, like conducting polymers, quinone units, and conjugated systems directly into the backbone of the COFs creates energy storage and electrochemically active COFs. Using chiral building blocks, chiral COFs can be constructed to be used in enantioselective separation and asymmetric catalysis. Porphyrin- and porphyrinoid-based COFs embed the light-harvesting and redox properties directly into the framework, providing inbuilt photochemical and catalytic properties. Hydrazone-linked COFs are reported to be a new type of COFs that feature the reversible/irreversible linkage chemistry, other than the conventional imine chemistry, and quinoline-linked COFs are more robust due to the irreversible linkage chemistry via the π-extension. The growing toolbox of available linker chemistries — such as imines, β-ketoenamines, boroxines, hydrazones and quinolines — provides a way to tune functional groups without compromising framework stability and crystallinity (Souto *et al*., 2020; Chen *et al*., 2020; Zhao *et al*., 2022).

The most frequently used organic linkages used for the synthesis of covalent organic frameworks (COFs) are summarized and compared in Table 4, along with their precursors, uses, and drawbacks. Boronic acids and boronic acids that have been functionalized with catechols are some of the earliest chemistries for COFs and are useful for the production of highly crystalline COFs with large surface area. Both, however, will hydrolyse and are sensitive to water, so these are not suitable for use in both aqueous and humid conditions (Tang *et al*., 2022). The condensation of aldehyde and amine provides the imine-linked COFs, which have been widely studied and used due to the simplicity of their synthesis, flexibility of their structure, and relatively good stability.

Table 4: Common Organic Linkages Used in COF Synthesis

Linkage	Processors	Advantages	Limitations
Boroxine	Boronic acids	High crystallinity	Moisture sensitive
Boronate ester	Boronic acids + Catechols	Large surface area	Hydrolysis
Imine	Aldehydes + Amines	Easy synthesis	Moderate stability
Beta-Ketoenamine	Aldehydes + Amines	Excellent chemical stability	Longer synthesis
Hydrazone	Hydrazides + Aldehydes	Good stability	Slower reaction
Triazine	Nitriles	High thermal stability	Requires harsh conditions

However, for the β-ketoenamine-linked COFs, longer synthesis times are required, but the resulting material shows excellent chemical and hydrolytic stability, making it suitable for harsh operating conditions. Hydrazone-linked COFs offer increased stability, but with slower reaction rates. On the other hand, the COFs in which the C–N bond is replaced by a C–N–N bond (triazine-linked COFs) are extremely thermally and chemically stable, but their synthesis is typically performed at high temperature or under harsh reaction conditions (Dubey *et al*., 2024; Guan *et al*., 2022; Wang *et al*., 2022)

4.4 Post-Synthetic Modifications

Post-synthetic modification (PSM) is a challenge-avoiding alternative to direct synthesis that can be used to functionalize COF with bulky groups that would otherwise hinder crystallization. Four main categories of PSM have been identified: (1) Post-functionalization where new functional groups are added by covalent bond formation, (2) Post-metalation which involves the insertion of metal centres/metal complexes in preformed frameworks, (3) Chemical locking in which the dynamic bonding is irreversible and the frameworks are crosslinked, and (4) Host-guest post-modifications, in which molecular cargo is introduced by non-covalent interactions. PSM approaches allow for the systematic modification of porosity, conductivity, hydrophobicity/hydrophilicity, chirality and other key properties with little change in crystallinity. Selective surface modification for enhanced gas separation performance, incorporation of photosensitizer and catalytic sites for enhanced photocatalytic activity, surface decoration of targeting ligands for targeted drug delivery and introduction of specialized binding groups for environmental remediation are among the applications of PSM. The versatility and adaptability of PSM strategies are key tools for optimizing COF performance in various applications (Segura *et al*., 2019; Liu *et al*., 2023; Yusran *et al*., 2020)

5. Storage and Conversion Applications

5.1 Supercapacitors and Batteries

Covalent organic frameworks (COFs) have emerged as highly promising electrode materials and active components for advanced electrochemical energy storage devices, including supercapacitors and rechargeable batteries. Their exceptionally high surface area, tunable porosity, ordered crystalline architecture, and tailorable electronic properties make COFs attractive alternatives to conventional carbon-based electrode materials (Li *et al*., 2020; Geng *et al*., 2020). In supercapacitors, electroactive

COFs containing intrinsic redox-active functional groups store energy through both electrical double-layer capacitance and pseudocapacitive charge-storage mechanisms, resulting in enhanced energy density and rate capability (Li *et al*., 2020). Nitrogen-rich COFs exhibit superior capacitive performance owing to improved electrical conductivity, abundant redox-active sites, and accelerated charge-transfer kinetics. In lithium-ion batteries, COFs have been extensively explored as high-capacity cathode and anode materials because their programmable porous architectures facilitate efficient lithium-ion transport and reversible electrochemical reactions (Li *et* al., 2020; Geng *et al*., 2020). Lithium storage occurs through a combination of surface adsorption and ion intercalation within ordered pore channels, enabling reversible capacities approaching theoretical values through rational redox chemistry and composite material engineering (Li *et al*., 2020). Furthermore, hybrid materials based on metal–organic frameworks (MOFs) and COFs, including transition metal coordination polymer composites, have demonstrated enhanced electrical conductivity, energy density, and cycling stability compared with individual materials (Li *et al*., 2020; Zhang *et al*., 2024). In lithium–sulfur batteries, COF-based structured sulfur hosts effectively suppress the polysulfide shuttle effect, thereby improving sulfur utilization, capacity retention, and long-term cycling stability (Li *et al*., 2020). In addition, conjugated COFs possess tunable electronic band gaps that facilitate rapid electron-transfer kinetics and ion diffusion, making them highly attractive electrode materials for next-generation high-rate energy storage systems (Geng *et al*., 2020; Zhang *et al*., 2024).

5.2 Hydrogen evolution and water splitting.

Covalent organic frameworks (COFs) have emerged as efficient photocatalysts and electrocatalysts for hydrogen evolution because of their high surface area, tunable electronic structures, extended π-conjugation, and abundant redox-active sites. Nitrogen doping, molecular engineering, and post-synthetic metal incorporation enhance visible-light absorption, charge separation, and catalytic efficiency, making COFs promising alternatives to precious-metal catalysts for sustainable hydrogen production through water splitting (Geng *et al*., 2020; Zhang *et al*., 2024).

5.3 CO_2 Reduction and Catalysis

COFs have demonstrated excellent potential for electrochemical and photocatalytic CO_2 reduction due to their ordered porous structures, high surface area, and tunable catalytic sites. These properties facilitate efficient CO_2 adsorption, rapid electron transfer, and selective conversion of CO_2 into value-added products such as carbon monoxide, formate, and hydrocarbons. Rational framework design and post-synthetic modification further improve catalytic selectivity and reaction efficiency (Li *et al*., 2024; Zhang *et al*., 2024).

5.4 Electroactive COF Design

Conductive COFs are developed by taking into account the presence of conjugated frameworks, nitrogenous structures, quinones, porphyrins, and conductive linkers. Such materials have a high capacity for charge transportation and electrochemical efficiency, thus being promising materials for fuel cells, electrocatalysis, battery systems, hydrogen generation, hydrogen peroxide formation, and singlet oxygen generation (Geng et al., 2020; Li *et al*., 2020).

5.5 Characterization of Covalent Organic Frameworks

Complete characterization is important for determining the success of the COF synthesis and analyzing the characteristics of their structure and functions. The PXRD technique is performed to determine the

degree of crystallization and the framework structure, while FTIR and solid-state NMR techniques are done to verify the covalent bonding. SEM and TEM techniques are done to study the morphology and porosity structure, BET technique is done to determine the surface area and porosity, TGA is performed to check the thermal stability, and XPS is done to analyze the elements in the compounds (Zhang *et al*., 2024; Geng *et al*., 2020).

Table 5: Characterization Techniques for COFs

Technique	Information Obtained
PXRD	Crystal structure
FTIR	Functional groups
Solid-state NMR	Chemical bonding
SEM	Surface morphology
TEM	Internal microstructure
BET Analysis	Surface area and pore size
TGA	Thermal stability
XPS	Surface elemental composition

6. Biomedical and Drug Delivery Applications

6.1 Drug Delivery Systems and Targeted Therapy

Covalent organic frameworks (COFs) have been shown to serve as excellent carriers for precision drug delivery by overcoming the shortcomings of conventional drug carriers, including poor water solubility, non-specificity, toxicity, and low bioavailability (Haase, Lotsch, & Freund, 2022; Geng *et al*., 2020). High surface area, permanent porosity, and atomically tailorable structures allow achieving high drug loading, sustained drug release, and molecule-level tuning for therapeutics (Haase *et al*., 2022; Zhang *et al*., 2024). The modularity of the COF structure allows adding targeting ligands by either the linker design or post-synthesis functionalization to realize targeted drug delivery. Moreover, various functional groups responsive to environmental stimuli, such as pH, light, and redox, can be installed to realize stimuli-responsive drug release (Haase *et al*., 2022). For example, COF nanocarriers modified with folate receptor ligands have been used for targeting and delivering anti-cancer drugs to the folate receptor-positive cancer cells. The all-carbon nature of COFs eliminates the risk of toxic metal ions associated with some metal–organic frameworks (MOFs), providing them with significant advantages in biomedical applications. Recent development in nanoparticles' fabrication techniques also makes it possible to synthesize nanoscale COFs capable of efficient systemic drug delivery with high drug loading and controlled release behavior (Haase *et al*., 2022; Zhang *et al*., 2024).

6.2 Biosensing and Detection

Inherent porosity, tunable electronic features, and versatile surface chemistry render COFs highly useful for biosensing and chemical sensing purposes (Geng *et al*., 2020; Zhang *et al*., 2024). COFs have found usage in explosive, moisture, pH, disease markers, toxic gas, VOCs, and metal ion sensing using selective adsorption and surface modification. Fluorescent and phosphorescent COFs provide a highly sensitive platform for real-time optical sensing through the variation in emission wavelength and intensity after analyte interaction. Besides, label-free sensors for the detection of bio-molecules using surface plasmon resonance (SPR) and molecularly imprinted polymers (MIPs) synthesized from

COF precursors furnish highly selective and sensitive analytical tools (Haase *et al*., 2022; Zhang *et al*., 2024).

6.3 Photodynamic Therapy and Imaging

COFs have been shown to be effective nanoplatforms for PDT because of the ability of these nanomaterials to incorporate porphyrin and porphyrinoid photosensitizers into highly porous frameworks. When exposed to light irradiation, COFs produce ROS, especially singlet oxygen, for targeted PDT of cancer. The porous structure of COFs promotes oxygen diffusion, and the nanosized particles enable deeper penetration of the material into the tumour tissue. Multifunctional COFs can incorporate not only PDT drugs but also various diagnostic tools, such as fluorescent or radioactive probes, allowing the use of COFs in the theranostic approach. Protonation of nitrogen-based COFs is an effective way to increase the photocatalytic activity of these materials and the production of singlet oxygen, improving the performance of PDT. Machine learning-assisted designing of materials has become an important tool in the development of new COF architectures for photodynamic and photothermal therapy, and combination therapies based on PDT and other approaches, such as chemotherapy or immunotherapy, proved to be effective (Haase *et al*., 2022; Zhang *et al*., 2024; Geng *et al*., 2020).

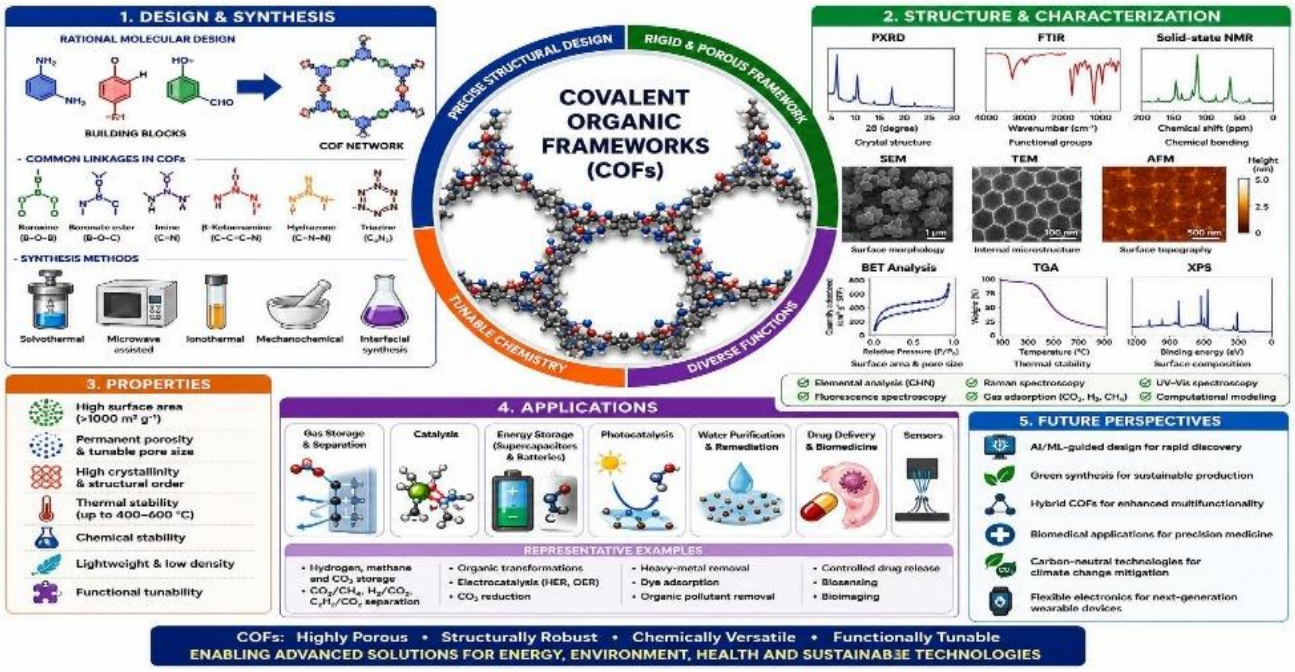

Figure 1: Schematic overview of Covalent Organic Frameworks (COFs)

6.4 Biocompatibility and In Vivo Applications

Development of biocompatibility and safety profiles of COFs are prerequisite for clinical translation of COF therapeutics. The complete organic character of COFs means that there are no worries about metal toxicity, which can arise in the development of MOFs, and their chemical stability in physiological conditions ensures their long-term activity in biological systems. Implementing cellular model characterization of COF nanoparticles shows minimal cytotoxicity compared to the conventional nanocarriers, where the processes of cell internalization involve endocytic pathways. Circulation half-life and the reticuloendothelial system uptake can be increased by surface modification with biocompatible polymers like hyaluronic acid or polyethylene glycol, which leads to an

enhancement of bioavailability for systemically injected COF nanoparticles (Geng *et al*., 2020). In vivo biodistribution studies show that targeted COF nanocarriers selectively target tumor tissues with low levels of accumulation in healthy off-target organs when they are equipped with the right targeting molecule. Very few studies have investigated the degradation pathways of COFs in biological environments, and the results indicate that degradation occurs via amide hydrolysis and oxidation reactions. The rational design of biodegradable COFs by introducing enzymatically cleavable linkages is an emerging area in the development of transient therapeutics with decreased long-term toxicity issues (Jiang *et al*., 2021; Zhang *et al*., 2024)

7. Environmental applications and challenges

7.1 Gas Storage and Separation

Covalent organic frameworks (COFs) are emerging as one of the most promising adsorbent materials for gas storage and separation applications, which are of critical importance for industrial, environmental and energy sustainability challenges. The traditional separation technologies like cryogenic distillation and compression are very energy-intensive, have high capital expenses, and are difficult to operate. Physical adsorption from porous materials, such as COFs, is very energy efficient, as there is no need for phase changes of the gases. To be used in fuel cell applications, hydrogen storage in COFs must be a function of hydrogen adsorption capacity, desorption kinetics and cycle stability. Under cryogenic conditions, hydrogen storage in COF structures can be optimized to have a capacity of over 10 wt%, and be made reversible. COF porosity optimization also applies to methane storage applications for natural gas utilization. Selective adsorption can be used to fractionate crude oil components and provide separation of valuable isomers by hydrocarbon separation. Carbon dioxide capture applications have been the subject of great attention, and COF adsorbents have shown to have the best performance in the both industrial point source capture and new direct air capture (DAC) technology. The CO_2 reduction rates that have been made possible by recent innovations are impressive for decoupled photosynthesis systems. The ability of COF to capture toxic gases such as SO2, SF6, and NH3 highlights its potential for various industrial and environmental applications. Mechanisms of separation are controlled by the differences in physisorption enthalpy, rate of physisorption, and selective pore accessibility. Further enhanced separation selectivity and capacity are achieved by strategically modifying the pore environment by post-synthetic surface-functionalization or by incorporating composites. The most important optimization strategies to improve storage or separation performance are the bottom-up synthesis approaches, PSM strategies, and interpenetration regulation (Jiang *et al*., 2021; Geng *et al*., 2020; Zhang *et al*., 2024). **Table 6** shows various uses of covalent organic frameworks (COFs) and the specific roles that they play along with the advantages of such frameworks. Due to their high surface area, tunable porosity, and chemical stability, COFs can act as adsorbents in gas storage, allowing for efficient storage of hydrogen, methane, and carbon dioxide. In gas separation, the ability to tune the pore size allows for efficient separation of different gases in industrial settings. When acting as catalyst supports, COFs have a lot of active sites and are structurally stable, which increases the effectiveness of the reactions performed on them and enhances the selectivity. As electrodes in supercapacitors and rechargeable batteries, COFs allow for high capacitance and fast charge transfer. Their porous structure and biocompatibility makes them effective drug delivery carriers, which allows for targeted release of drugs. Furthermore, COFs are commonly used as adsorbents in water purification systems because they are able to remove dyes, heavy metals,

and other contaminants from water. Also, COFs can be used in biosensing due to their sensitivity and selectivity (Geng *et al*., 2020; Zhang *et al*., 2024).

Table 6: Major Applications of COFs

Applications	Role of COFs	Benefits
Gas storage	Adsorption	High capacity
Gas Separation	Selective adsorption	High efficiency
Catalysis	Catalysts support	High activity
Super capacitors	Electrode material	High capacitance
Batteries	Electrode	Improved cycling stability
Drug Delivery	Carrier	Controlled release
Water Purification	Adsorbent	Pollutant removal
Biosensors	Sensing platform	Pollutants removal

7.2 Water Treatment and Adsorption

Water purification remains one of the most pressing global challenges, and covalent organic framework (COF)-based materials have emerged as highly promising candidates because of their exceptional physicochemical properties and significant environmental and public health benefits (Desai *et al*., 2024; Zhang *et al*., 2024). COFs exhibit outstanding performance in the removal of a wide range of water pollutants, including organic dyes, heavy metal ions, pharmaceutical residues, and persistent organic pollutants, through multiple adsorption mechanisms such as pore filling, electrostatic interactions, π–π stacking, hydrogen bonding, and coordination interactions (Zhang *et al*., 2024). COF adsorbents have demonstrated nearly complete removal of methylene blue from textile wastewater together with excellent regeneration and reusability, highlighting their potential for industrial wastewater treatment and water recycling. For heavy metal remediation, functionalized COFs containing chelating groups such as thiol, amino, and imine moieties exhibit high affinity and selectivity toward toxic metal ions including Pb^{2+}, Hg^{2+}, Cr(VI), and radioactive metal ions (Desai et *al*., 2024). In particular, thiol-functionalized COFs have shown exceptional mercury adsorption capacity and selectivity, greatly outperforming many conventional adsorbents (Huang *et al*., 2022). Nitrogen-rich COFs have also demonstrated efficient removal of anionic dyes such as indigo carmine through electrostatic attraction and surface functionalization (Zhang *et al*., 2024). The high specific surface area, ordered pore channels, and tunable pore architecture of COFs facilitate rapid contaminant diffusion and superior adsorption kinetics, resulting in enhanced mass-transfer performance compared with conventional adsorbent materials (Jiang *et al*., 2021). Furthermore, recent advances in room-temperature and green synthetic strategies have enabled more sustainable and scalable production of COF adsorbents with reduced environmental impact (Desai *et al*., 2024). The incorporation of COFs into membrane filtration systems has also led to the development of high-performance hybrid

separation platforms that combine molecular sieving with selective adsorption, thereby achieving superior purification efficiency beyond conventional size-exclusion mechanisms (Zhang *et al*., 2024).

7.3 Direct Air Capture of CO2

DAC is a relatively new carbon capture technology with great potential to reduce CO_2 emissions and generate net-negative emissions by capturing CO_2 directly from the atmosphere and storing it in geological formations or using it for beneficial purposes, such as carbon utilization (Sanz-Pérez *et al*., 2016; Fasihi, Efimova, & Breyer, 2019; Keith *et al*., 2018). The selective extraction of CO_2 from air is much more difficult than the selective extraction of CO_2 from concentrated industrial flue gas streams, which is why DAC is particularly challenging (Fasihi *et al*., 2019). Hence, the adsorbent materials used in DAC should have extremely high CO_2/N_2 selectivity, fast adsorption–desorption rate, high adsorption capacity at very low CO_2 partial pressure and low regeneration energy requirement (Li *et al*., 2024). Superior DAC performance has been shown for porous carbon materials doped with nitrogen and hybrid metal–organic framework (MOF)/covalent organic framework (COF) composites; computational modelling, high throughput screening and machine learning have all been used to discover and optimise next-generation adsorbents (Li *et al*., 2024; Jiang *et al*., 2021). The detailed investigations of the adsorption of low-concentration CO_2 on porous solid adsorbents have helped to gain insight into adsorption mechanisms, diffusion behaviour and catalytic conversion pathways and thus enabled rational material design (Zhang *et al*., 2024; Li *et al*., 2024). In addition, solar-assisted sorbent regeneration is a potential solution to use less energy and carbon footprint in DAC systems. Combination of DAC and downstream catalytic CO_2 conversion process can be used to convert CO_2 from capture to value-added chemicals and synthetic fuels, which can help to create circular carbon economy (Li *et al*., 2024). Advanced porous materials, especially COFs, have been shown to have outstanding potential to improve the adsorption performance and selectivity, and their energy efficiency, and are projected to be a key driver in making future DAC-based carbon management strategies (CMMS) technically and economically viable (Jiang *et al*., 2021; Zhang *et al*., 2024).

7.4 Scalability and Industrial Translation

Despite significant advances in the science of covalent organic frameworks (COFs), moving these materials beyond the demonstration stage to industrial scale production and commercialization is still very challenging (Freund *et al*. 2021; Desai *et al*. 2024). The current production methods are primarily batch synthesis, but this approach has many limitations, such as poor reproducibility, inefficient use of resources, and scalability (Desai et al., 2024; Zhang *et al*., 2024). To enable scalable synthesis with a consistent crystallinity, porosity, and integrity of functional groups, significant advances in process control, reaction engineering, and characterization methodologies are needed (Jiang *et al*., 2021; Zhang *et al*., 2024). However, for industrial production, there are various challenges to overcome, such as the development of low-cost monomer precursors, optimization of reaction time and solvent use to bring down the production cost, and implementation of continuous flow synthesis for continuous production (Desai *et al*., 2024; Freund *et al*., 2021). Recent progress in mechanochemical and room-temperature aqueous synthesis methods provides potential methods for the environmentally friendly and economically viable large-scale production of COFs (Desai *et al*., 2024). Moreover, it is crucial to have standardized processes for COF synthesis, characterization, and performance testing to enable commercialization and regulatory approval (Zhang *et al*., 2024). Comprehensive life-cycle assessment (LCA) and techno-economic analysis (TEA) are still limited and important to compare the environmental and economic feasibility of COF with traditional materials (Desai *et al*., 2024).

However, for biomedical and environmental applications, long-term stability tests under realistic operating conditions and comprehensive toxicity tests are needed to support the regulatory process and safe commercialization (Freund *et al*., 2021; Zhang *et al*., 2024). However, for successful commercialization, there is a need for comprehensive and close cooperation between academia and industrial producers as well as regulatory bodies and end-user industries in order to transfer technologies and facilitate the production of COF based products in large scale (Jiang *et al*., 2021; Desai *et al*., 2024).

Table 7: Recent Applications of COFs (2021–2026)

Application area	Recent Advances
Energy storage	Flexible batteries and supercapacitors
Photocatalysis	Hydrogen production
Environmental remediation	Heavy-metal removal
Carbon capture	Enhanced CO_2 adsorption
Biomedical applications	Cancer therapy and drug delivery
Chemical sensing	Ultra-sensitive biosensors
Flexible electronics	Organic electronic devices

Table 7 presents the key developments in the utilization of covalent organic frameworks (COFs) from 2021 till 2026. The rapid development of these materials is evident in various technological applications. In the area of energy storage, COFs have become promising constituents of flexible batteries and high-performing supercapacitors due to their porosity, controllable structure, and excellent electrochemical properties. In the sphere of photocatalysis, there were notable advancements in the use of COFs for effective production of hydrogen under sunlight to develop sustainable energy technologies. In the sphere of environmental remediation, modified COFs have become highly effective in the removal of toxic heavy metals and organic compounds from contaminated water. There was also considerable improvement in the development of techniques for capturing carbon dioxide to mitigate climate changes. In the sphere of biomedicine, COFs have proven their applicability in drug delivery and cancer treatment through controlled release. Moreover, the latest developments in chemical sensing led to the creation of highly sensitive biosensors. Lastly, there was advancement in the sphere of organic electronics, which allowed for the creation of innovative wearable devices (Jiang *et al*., 2021; Desai *et al*., 2024).

8. Future Perspectives

Covalent organic frameworks (COFs) are one of the most promising and rapidly evolving families of crystalline porous materials that have been shown to be useful for applications including energy storage and conversion, biomedical drug delivery, environmental remediation, catalysis and chemical sensing (Freund *et al*., 2021; Desai *et al*., 2024). To continue advancing in this area, synthetic chemistry, computational design, advanced materials characterization and device engineering are needed to speed up the development of next-generation COFs (Jiang *et al*., 2021; Zhang *et al*., 2024). The future research directions are: (1) robust, scalable, and economically viable synthetic methodologies for industrial synthesis; (2) advanced reticular design strategies for constructing COFs with enhanced

electronic, optoelectronic, and catalytic properties; (3) extensive biological safety and biocompatibility testing for clinical translation; (4) integration of machine learning and artificial intelligence for accelerated materials discovery, structure prediction, and performance optimization; and (5) pilot-scale production and commercialization of market-ready COF based technology (Desai *et al*., 2024; Zhang *et al*., 2024). In addition, there are growing opportunities for COF to be combined with other materials that share similar porous properties, such as metal–organic frameworks (MOFs), MOF/COF hybrid structures, and other porous polymers, to create multifunctional hybrid materials with synergistically increased physicochemical properties that are superior to those of their individual constituents (Freund *et al*., 2021; Hao *et al*., 2024). **Table 8** provides an overview of the future research directions expected to affect the future of covalent organic frameworks (COFs). It is expected that the use of artificial intelligence (AI)-guided design will enhance the creation and improvement of COF materials by offering faster predictions of material properties and performances. There is increasing focus on green chemistry for developing eco-friendly, energy-efficient, and scalable COF manufacturing. Hybrid COFs made from metal, polymer, or nanomaterials are expected to offer increased functionalities and expand applications such as catalysis, sensing, and energy storage. Biomedical applications of COFs involve the use of advanced COFs in precision medicines such as drug delivery, bioimaging, and therapy systems. COFs are also expected to make great contributions to carbon-neutral technologies through capturing carbon dioxide, energy generation, and hydrogen production in the efforts against climate change. In addition, the use of COFs in flexible electronics is likely to revolutionize future electronics through lightweight and wearable electronic devices (Freund *et al*., 2021; Hao *et al*., 2024).

Table 8: Future Trends in COF Research

Research Direction	Expected Impact
Artificial intelligence-guided design	Faster material discovery
Green synthesis	Sustainable production
Hybrid COFs	Enhanced multifunctionality
Biomedical applications	Precision medicine
Carbon-neutral technologies	Climate change mitigation
Flexible electronics	Next-generation wearable devices

Conclusion

Covalent organic frameworks (COFs) are a versatile family of crystalline porous materials, possessing exceptional structural tunability, high surface area, and excellent chemical stability. The recent advances in synthetic methods and rational design strategies have paved the way for the construction of COFs with tailored pore architectures, improved functionalities, and enhanced performance in a wide range of applications. Their unique properties make them promising candidates for gas storage and separation, catalysis, energy storage and conversion, environmental remediation, sensing, and drug delivery. While much progress has been achieved, challenges such as scalable synthesis, long-term stability under practical conditions, and cost-effective production remain. Innovative design and interdisciplinary research to overcome these limitations will further accelerate the translation of COFs from laboratory studies to large-scale industrial and biomedical applications.

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