### REVIEW



### Covalent organic frameworks: a review of synthesis methods, properties and applications for per- and poly-fluoroalkyl substances removal

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### Abstract

Adsorption using covalent organic frameworks (COFs) is very effective and favoured for removing per- and polyfluoroalkyl substances (PFAS) from various matrices. The prominent classes of COF, their synthesis methods, and their application in COF-based technologies for PFAS adsorption in myriad environments are discussed. Furthermore, the influencing PFAS adsorption characteristics of the distinct COF classes are also examined. COFs have large specific surface areas and porosity, offering PFASs a host of adsorption sites and thus high adsorption capabilities.  $\beta$ -Cyclodextrin-based COFs ( $\beta$ -CD-COFs), ionic COFs (iCOFs), amine-functionalised COFs, porphyrin-based COFs and hydrophobic COFs are some of the most notable examples of COFs and as such have been employed for large-scale PFAS remediation. Direct and post-synthetic modification are the two main COF design methodologies. The general approach in constructing various frameworks involves the reaction of ion monomers with other neutral monomers. For COFs, solvothermal synthesis is currently the main direct synthetic method. The process used to synthesise COFs tremendously impacts how effectively they adsorb PFAS. High-performance materials for PFAS remediation are created by researchers by customising COF characteristics and using suitable synthesis techniques. The authors' objective is to give readers and researchers alike a broad overview of the current status of COF research and development, including numerous challenges and prospects associated with the adsorption of PFASs by COFs.

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### **Graphical abstract**

Application of Cement Stabilized OB dump, BOF slag, Fly Ash Mixes asSustainable Pavement Material



**Keywords** COFs ·  $\beta$ -Cyclodextrin-based COFs · ICOFs · Amine-functionalised COFs · Porphyrin-based COFs · Hydrophobic COFs

### Introduction

Covalent organic frameworks (COFs) are porous materials with regular pore structures, strong stability, and structural designability (Abuzeid et al. 2021). COFs have outstanding selectivity for targets (Tang et al. 2022), fast mass transfer, and better adsorption capacity compared to commercial adsorbents like C18 (Sun et al. 2021). Different functionalised COFs, such as ionic COFs (iCOFs) and fluorine-functionalised COFs, are now being used for the adsorption of PFASs (Tang et al. 2022). However, because of their innate hydrophobicity, they are more difficult to disperse in the extraction solution, which reduces the extraction efficiency (Zeppuhar et al. 2023). On the other hand, iCOFs overcome the drawbacks of fluorine-functionalised COFs due to their excellent dispersion in the extraction solution in addition to their ability to adsorb PFASs. However, they frequently suffer from a lack of selectivity when trying to recover trace PFASs from complicated mixtures (Zeppuhar et al. 2023). Synthesis of bifunctional COFs with both fluorine and quaternary ammonium groups is very desirable to overcome these obstacles. More functional groups and active sites, as well as quicker sorbate diffusion rates, are made possible by COFs' large specific surface area (Hou et al. 2020a).

Per- and polyfluoroalkyl substances (PFAS) are a class of man-made chemicals composed of hundreds of molecules. They have strong carbon-fluorine linkages, which make them exceedingly stable, resistant to degradation (Ross et al. 2018), and long-lasting in the environment (Olsen 2015). PFAS have been widely employed in industrial and consumer products because of their unique qualities, which include water and oil resistance, chemical stability, and surfactant capabilities (Ross et al. 2018; Olsen 2015). However, PFAS exposure has been related to negative health consequences in humans, including developmental effects, immune system issues, and endocrine disruption (Cohn et al. 2020). PFAS can interfere with hormone function, potentially altering metabolism, growth, and reproductive health. Some studies have revealed that PFAS exposure may raise the risk of some malignancies, including kidney and testicular cancer (Singh et al. 2023).

The removal of PFAS from polluted environments is a complex and difficult undertaking due to their resistance to degradation and ubiquitous presence in diverse matrices. Adsorption with porous materials such as activated carbon (Park et al. 2020), biochar (Issaka et al. 2022), and ion exchange resins (Umeh et al. 2023) have been used to remove PFAS from polluted water and soil. PFAS molecules adhere to the surfaces of these matrixes, which may then



Fig. 1 Summary of structural diversity of various examples of COFs (Lohse et al. 2018). Reproduced with permission. License copyright 2018 WILEY-VCH

be filtered and disposed of; their efficacy varies depending on the adsorbent material and PFAS characteristics (Bei et al. 2014). Owing to the chemical structure and functional groups of certain PFAS compounds or classes, COFs can be designed to display preferential affinity towards them (Sharma et al. 2024). Targeting distinct PFAS molecules with high affinity and specificity, selective binding sites may be created by adjusting the COF framework's pore size, surface chemistry, and intermolecular interactions (Zahmatkesh et al. 2024). Adsorbed PFAS molecules can be removed from the COF surface using regeneration techniques such as solvent washing or heat treatment, which will restore the surface's ability to sense or adsorb substances (Calore et al. 2024).

Based on the adsorption characteristics of COFs, Zarei et al. (Zarei et al. 2024) described the synthesis and study of COF-I, a novel COF with a high affinity for PFAS adsorption. COF-I was synthesised and completely characterised using the condensation process of 2,4,6-trimethyl-1,3,5-triazine with 2,3-dimethoxyterephthaldehyde. In addition to its high crystallinity and surface area, COF-I demonstrated excellent hydrolytic and thermal stability. The researchers assessed the crystallinity of both COFs using X-ray diffraction (XRD) and used atomistic simulations coupled with cross-polarisation/magic angle spinning solid-state nuclear magnetic resonance (CP/MAS ssNMR) to identify the relative quantities of AA-stacking and AB-stacking present. COF-I, with its hydrophobic surface and methoxy groups in the ortho positions, exhibited the highest PFAS adsorption (Zarei et al. 2024). Besides, Wang et al. (Wang et al. 2021a) created four  $\beta$ -cyclodextrin COFs ( $\beta$ -CD-COFs) that effectively remove and adsorb four distinct PFSAs in water. All  $\beta$ -CD-COFs displayed rapid adsorption for PFSAs with high adsorption capacities (0.33–1.51 mmol/g), which were much superior to those of typical resins and activated carbons, most likely due to the ordered pores of  $\beta$ -CD-COFs and the electron-deficient cavity  $\beta$ -CD (Wang et al. 2021a).

Over the last few decades, innovative methods have been developed to remove PFASs by an adsorption process. In addition, several critical reviews that focus on distinct PFAS sources, types, and characteristics (Walkowiak-Kulikowska 2022), as well as PFAS removal in diverse environments, have been published in recent years (Sharma et al. 2024). Previous scientific literature concentrated on advanced oxidation processes (AOPs) (Issaka 2024; Issaka et al. 2024), membrane filtering technologies (Adams et al. 2024), and in situ treatment approaches for PFAS cleanup. Moreover, several studies provide a full discussion of distinct COFs and their respective preparation procedures (Zarei et al. 2024). However, to the best of our knowledge, no review paper has provided a compressively up-to-date review of COF for PFAS remediation. This paper thus covers the major classes of COF, their synthesis procedures, as well as their application in COF-based technologies for PFAS adsorption in water and soil settings. This manuscript further discusses the properties of the myriad COF classes for PFAS adsorption. This review provides an overview of the current state of COF research and development, highlighting achievements in knowledge, process technology, and PFAS removal applications. Finally, we conclude with the multiple challenges and prospects associated with COFs-mediated PFAS adsorption.

# Classes and synthesis methods of covalent organic frameworks (COFs)

COFs such as  $\beta$ -cyclodextrin-based COFs ( $\beta$ -CD-COFs), iCOFs, amine-functionalised COFs, porphyrin-based COFs, and hydrophobic COFs have demonstrated high adsorption capacities and selectivity for removing PFAS from contaminated water, leading to the development of large-scale strategies. This section discusses the synthesis methods of the various classes. Figure 1 summarises various structural diversity in COFs.

# $\beta$ -Cyclodextrin-based covalent organic frameworks ( $\beta$ -CD-COFs)

A type of porous material,  $\beta$ -CD-COFs are created by combining  $\beta$ -cyclodextrin molecules into the framework structure (Chen et al. 2024). A cyclic oligosaccharide,  $\beta$ -cyclodextrin, is made up of seven glucose units connected by  $\alpha$ -1,4-glycosidic bonds. It has a unique toroidal shape with a hydrophobic cavity and a hydrophilic outer surface, which enables it to form inclusion complexes with diverse guest molecules, showing high adsorption capacities and rapid removal rates for PFSAs in water (Wang et al. 2024a).  $\beta$ -Cyclodextrin serves as a fundamental component of  $\beta$ -CD-COFs, forming an organised and porous network through its connections with other organic linkers (Xue et al. 2024).  $\beta$ -CD-COFs are usually synthesised by a solvothermal or microwave-assisted method that employs precisely engineered precursors and reaction conditions. The resultant frameworks have exceptional stability, large surface areas, and adjustable pore diameters, among other special features.

Because  $\beta$ -cyclodextrin is present in the framework, it may form inclusion complexes with guest molecules, which opens up possibilities for applications such as selective adsorption, separation, and sensing (Sahu et al. 2023).



Fig. 2 Schematic fabrication of  $Fe_3O_4@COF@\beta$ -CD and MSPE technique for determining oestrogens and oestrogen mimics (Liu et al. 2022). Reproduced with permission. License number 5863631408608

Furthermore, because  $\beta$ -cyclodextrin is a chiral molecule,  $\beta$ -CD-COFs can display enantioselective qualities, which makes them appropriate for chiral separation and catalysis.  $\beta$ -Cyclodextrin's hydrophilic outer surface and hydrophobic interior combine to give  $\beta$ -CD-COFs their amphiphilic character, which is advantageous for uses including drug administration and biomolecule immobilisation (Antipova et al. 2024).  $\beta$ -CD-COFs are a flexible family of materials that combine the benefits of  $\beta$ -cyclodextrin and COFs. Their distinct characteristics render them auspicious contenders for an array of uses, encompassing medication administration, chiral separation, gas storage and separation, and sensing. It is anticipated that more investigation into the synthesis, characterisation, and utilisation of  $\beta$ -CD-COFs will yield novel findings and progress in the domain of porous materials.

### Thiol-ene click strategy for the synthesis of $\beta$ -CD-COFs

The thiol-ene click technique is an effective way to synthesise functionalised COFs, including  $\beta$ -CD-functionalised COFs (Li et al. 2019). This approach comprises the interaction of a thiol group (containing a sulphur atom) with an alkene (a carbon–carbon double bond) in the presence of a radical initiator, usually under moderate reaction conditions (Li et al. 2019; Wang et al. 2023a). During this technique, the COF is synthesised using a suitable organic precursor and a synthetic method, such as solvothermal or microwaveassisted synthesis. The  $\beta$ -CD molecule is functionalised with a thiol group, typically through a substitution reaction involving a thiol-containing reagent, such as cysteamine or 2-iminothiolane. The thiol-functionalised  $\beta$ -CD and the COF-containing alkene groups are mixed in a suitable solvent in the presence of a radical initiator, such as azob. The thiol-ene click reaction creates a persistent thioether bond between the  $\beta$ -CD and COF by reacting thiol and alkene groups (Liu et al. 2023a). Szymańska et al. (Szymańska et al. 2024) proposed a fast and efficient method for synthesising a library of organo-functional alkoxysilanes using an amine-catalyzed thiol-isocyanate click reaction. The thiolene reaction produced new thiols and thioacetates, which were then reduced to thiols. Alkoxysilanes were synthesised via two routes: the reaction between 3-isocyanatopropyltriethoxysilane (ICPTES) and functional-group-containing thiols or between 3-mercaptopropyltriethoxysilane (MPTES) (Szymańska et al. 2024).

Owing to the effectiveness of the thiol-ene click technique for the preparation of a myriad of organosilicon compounds (Szymańska et al. 2024), it was presented by Liu et al. (Liu et al. 2022) to synthesise a new  $\beta$ -CD-COF-based magnetic nanocomposite (Fe<sub>3</sub>O<sub>4</sub>@COF@ $\beta$ -CD) (Fig. 2), which were subsequently applied as adsorbents for magnetic solid-phase extraction (MSPE) of oestrogens and oestrogen mimics. Fe<sub>3</sub>O<sub>4</sub>@COF@ $\beta$ -CD exhibits superparamagnetism, a high surface area, and superior adsorption of oestrogens and oestrogen mimics. Under optimised circumstances, the new technique achieved good linearity ( $R^2 > 0.9989$ ) and low limits of detection (0.9–3.4  $\mu$ g kg<sup>-1</sup>). The MSPE-HPLC-FLD technique was successfully used on genuine milk and meat samples, with recoveries ranging from 89.0 to 105.4% and RSDs < 5.7% (Liu et al. 2022). Besides,  $\beta$ -CD is a promising chiral carrier for several applications due to its outstanding chiral recognition capabilities. Chen et al. (Chen et al. 2024) used a solvothermal approach to create a porous COF-V, and

ICOF synthesis techniques	Advantages	Disadvantages	Refs	
Direct synthesis: Solvothermal synthesis, microwave synthesis, mechanochemi- cal synthesis and room temperature synthesis	Strong controllability over shape, crystal- linity, and porosity; broad application; high productivity	High pressure and temperature; protracted synthesis time	Ben et al. (2024b); Hayat	
	Quick synthesis time; great output; Environmental preservation and energy conservation	High standards for the reaction vessel; Limited applicability	et al. (2024)	
	environmental friendliness, simplicity and high efficiency, ease of operation and scaling up, and simplicity in reaction control	Limited purity of the product; low crys- tallinity		
	Lower energy usage, safe operation, and mild reaction conditions Adequacy for materials that are sensitive to tempera- ture	Low repeatability, restricted crystallinity, and sluggish response rate		
Post-synthetic modification: coordination- based modification	High crystallisation quality; good ionisa- tion features; simplicity in synthesis; flexibility and variety	Multiple-step synthesis method; possible influence on stability	Segura et al. (2019); Rejali	
	Cost-effectiveness, structural stability, and high controllability	Critical synthesis condition; restricted modification places	et al. (2023)	

Table 1 The benefits and drawbacks of the two primary iCOF synthesis techniques (Direct synthesis and post-synthetic modification)

 $\beta$ -CD was modified in two steps to create mercapto- $\beta$ -CD ( $\beta$ -CD-SH). Next, a  $\beta$ -CD-based COF (COF-S-CD) was synthesised using a thiol-ene "click" reaction. COF-S-CD was successfully used for enantioselective liquid–liquid extraction of five racemic aryl carboxylic acids: 2-phenyl propionic acid, 2-(4-methyl phenyl) propionic acid, 2-(3-chlorophenyl) propionic acid, 2-(4-nitrophenyl) propionic acid, and  $\alpha$ -cyclohexyl mandelic acid (Chen et al. 2024).

Leveraging the distinct features of both  $\beta$ -CD and COFs, the synthesised  $\beta$ -CD-functionalised COF may subsequently be used for a range of applications, including chiral recognition, drug administration, and sensing. To further optimise the material's qualities for certain uses, more alterations might be made.

### Ionic covalent organic frameworks (iCOFs)

A distinct family of COFs known as iCOFs has ionic elements in their structural composition (Herath et al. 2022) that contribute further functionality and characteristics, while the organic building blocks are joined by covalent bonds (Ben et al. 2024a). Ionic functions, charged organic linkers, or ionic components can all be added to the COF structure to add ionic groups. Because of their ability to promote ion transport, iCOFs have attracted attention as possible materials for energy storage, electrochemical sensing, and membrane-based separations (Zou et al. 2022). In environmental remediation and water treatment, the charged nature of iCOFs can facilitate the selective adsorption and separation of charged molecules, including dyes, heavy metals, and ionic contaminants (Herath et al. 2022). Ionic interactions have the potential to improve the overall stability of iCOFs, increasing their resistance to deterioration and enhancing their functionality across a range of applications. By altering the kind and quantity of ionic components, iCOFs' qualities may be changed, offering the chance to optimise their performance for particular uses (Ben et al. 2024a; Zou et al. 2022).

Ionic building blocks that can form covalent bonds with other components during the COF synthesis process are designed and synthesised (Singh et al. 2024), and ionic functional groups are introduced onto the COF structure through chemical modifications or grafting techniques (Li et al. 2024a). ICOFs are synthesised by incorporating ionic groups through post-synthetic ion exchange with precursor COFs containing exchangeable counterions (Al-dolaimy et al. 2024). Besides, iCOFs are a promising subclass of COFs with special qualities and prospective uses in a range of industries, including chemical separations, energy storage, and environmental remediation. It is anticipated that more investigation into the synthesis, characterisation, and uses of these materials will progress in the area of porous materials.

### Strategies for the synthesis of ICOFs

Ionic components are incorporated into the COF structure by a variety of techniques to create iCOFs. Chemically induced dynamic covalent chemistry (DCC) is primarily used in the synthesis of long-range and organised intercalated fermions (iCOFs) (Ben et al. 2024b). Reversible processes appear to be essential for the construction of crystalline COFs because they enable mistake correction and self-healing, which stop amorphous products from forming. It is possible to modify and regulate the shape and characteristics of iCOFs by choosing suitable synthesis techniques. Direct synthesis and post-synthetic modification are the two main iCOF design methodologies, based on the DCC. The benefits and drawbacks of post-modification and direct synthesis are mentioned in Table 1 below.

### Direct synthesis of iCOFs

Ionic building blocks comprising charged organic moieties are developed and synthesised in the direct synthesis of iCOF technique (Ben et al. 2024a). To create iCOFs with the required ionic functions, these building blocks can subsequently combine with other substances through condensation or other covalent bond-forming processes. With this method, the kind and distribution of ionic groups inside the COF structure may be precisely controlled (Zhang et al. 2021). Direct synthesis is now the most often utilised technique for creating iCOFs. Generally speaking, ion monomers are used by researchers to react with other neutral monomers to build different topological configurations. The iCOFs may be constructed by pre-designing ion monomers and co-polymerising them with other monomers in DCC (Ben et al. 2024b). Moreover, the placements and concentrations of charges inside the frameworks are tunable. Room temperature, microwave-assisted, solvothermal, and mechanochemical are the predominant types of direct synthesis methods.

### Solvothermal synthesis of iCOFs

For the majority of reported iCOF, solvothermal synthesis is presently the primary synthetic technique. High pressure and temperature conditions are often needed for the reversible processes that create COF materials (Yu et al. 2024). Solvothermal synthesis, in contrast to other synthetic techniques, offers a closed system, high pressure, and constant temperature that are favourable to the reaction conditions for crystal formation. This enables the fabrication of iCOF materials with large surface areas and crystallinity. For the synthesis of iCOF, the choice and mix of solvents are essential (Ben et al. 2024b). The employment of various



Fig. 3 Schematic illustration of the mechanochemical synthesis of iCOF/cotton composites and its application in the pipette tip solid-phase extraction of domoic acid in seafood (Zambzickaite et al. 2022). Reproduced with permission. License number 5865730412026

solvents frequently results in various reaction pathways and processes, which have a significant impact on the yield, morphology, and crystallinity of the end products. Because of this, throughout the synthesis process, the solubility of the reaction monomers may be used to select solvent types, solvent ratios, and reaction pressure that will regulate the reaction's progress and product yield, ultimately regulating crystal development (Ben et al. 2024b; Yu et al. 2024). While extremely slow reaction rates may have an effect on the entire reaction process and result in reduced yields, excessively fast reaction speeds may cause more crystal defects, partial framework breaking, poor crystallinity, and excessive polymerisation. Zhang et al. (Zhang et al. 2018) created a simple, template-free solvothermal technique as a bottom-up strategy to easily and scalable create mesoporous/macroporous MOF nanosheets. It was discovered that the regulated development and shape of MOF crystals were mediated by beginning coordination complexes of various copper(II)-ligand compounds. It was shown that the structure and performances of the assemblies may be modified and tailored by varying the size and shape of the MOF crystals (Zhang et al. 2018).

#### Mechanochemical synthesis of iCOFs

By using mechanical forces, such as ball milling or grinding, mechanochemical synthesis of iCOFs can produce iCOFs with little or no solvent present (Bhambri et al. 2022). High-energy settings are necessary for this technique, such as grinding or ball milling, where mechanical forces create reactive conditions and speed up the reaction process. Consequently, mechanochemical synthesis frequently makes it possible to synthesise COF materials reasonably quickly and in a shorter amount of time. Besides, in about 30 min, iCOF@cotton (iCOF@cotton) was easily created using a mechanochemical grinding process by Wang et al. (Wang et al. 2024b) and employed it as an adsorbent for pipette tip solid-phase extraction (PT-SPE) (Fig. 3). With its high specific surface area, appropriate pore structure, and cationic charge groups of iCOF, the synthesised iCOF@cotton was able to rapidly extract polar targets. Additionally, the use of cotton helped to mitigate the issue of PT-SPE's high back pressure, which sped up the extraction process (Wang et al. 2024b).

The use of toxic solvents, extended reaction times, and high reaction temperatures in traditional solvothermal synthesis defy green chemistry principles. To address these challenges, Brown et al. (Brown et al. 2023) demonstrated for the first time the green, efficient, liquid-assisted mechanochemical synthesis of COF adsorbents with high iodine capacity. The ball milling synthesis was carried out at ambient temperature with varied liquid additives, generating six imine-linked COFs with varying pore sizes and functionalities in under one hour. After 1 min of ball milling, a typical COF showed high crystallinity and a surface area of 1387 m<sup>2</sup> g<sup>-1</sup>. This mechanochemical technology will lead the way for green, quick, simple, and scalable COF



**Fig.4** (I) Schematic illustration of **A** facile microwave-assisted synthesis of Mw-TFB-BD-X COFs under air in 1 h and space-filling models of **B** Mw-TFB-BD-CH<sub>3</sub> and **C** Mw-TFB-BD-OCH<sub>3</sub> with Layers Arranged in an Eclipsed Stacking Mode. (II) Time-dependent gravimetric iodine vapour adsorption of **A** Mw-TFB-BD-CH<sub>3</sub> and oven-TFB-BD-CH<sub>3</sub>; **B** Mw-TFB-BD-OCH<sub>3</sub> and oven-TFB-BD-OCH<sub>3</sub>

at 75 °C. Inset: Photographs of COFs before and after iodine vapour adsorption. **C** Static iodine adsorption capacities of Mw-COFs in this work and previously reported high-performing COF adsorbents. **D** Cycling performances of Mw-TFB–BD-CH<sub>3</sub> and Mw-TFB-BD-OCH<sub>3</sub> (Alsudairy et al. 2023). Reproduced with permission. License under CC-BY-NC-ND 4.0



**Fig.5** (I) **a** Schematic illustration of the room temperature synthesis of RT-iCOF through the condensation of Tp and Vio-NH<sub>2</sub>; **b** unit cells of the ABC-staggered model of RT-iCOF; **c** side view of the ABC-staggered model of RT-iCOF; **d** space-filling model of RT-iCOF in ABC-staggered model (grey, white, red, blue and green represent C, H, O, N, and Cl, respectively). (II) **a** Adsorption kinetics of RT-iCOF for DCF; **b** PSO kinetics adsorption linear fitting plots

synthesis, presenting exciting possibilities for applications in environmental remediation and beyond.

### Microwave-assisted synthesis of iCOFs

The quick synthesis of iCOFs utilising other energy sources such as mechanochemistry (Wang et al. 2024b), electron beam, and sonochemistry has sparked intense scientific interest over the last decade since the slow solvothermal synthesis presents significant barriers to their future uses (Zhang et al. 2018). Microwave-assisted synthesis has grown in popularity because of its inherent benefits over traditional solvothermal procedures, such as better yield (Alsudairy et al. 2023), reduced energy consumption, and enhanced physicochemical qualities of products (Ji et al. 2020). Conventional solvothermal synthesis necessitates multiday synthetic timeframes and anaerobic conditions, limiting its practical use. Alsudairy et al. (Alsudairy et al. 2023) demonstrated a simple microwave-assisted synthesis of 2D imine-linked COFs, Mw-TFB-BD-X in the air within 1 h (Fig. 4I). The resulting COFs had greater crystallinity, better yields, and more uniform morphology than their solvothermal counterparts. The as-prepared ICOF demonstrated remarkable iodine adsorption capabilities (Fig. 4II)

of DCF with different initial concentrations; **c** and **d** contribution of the PFO rate and the PSO rate in adsorption process; **e** Adsorption isotherms of RT-iCOF for DCF from 25 °C to 55 °C, solid line for Langmuir model and dashed line for Freundlich model; **f** Fitting plots of adsorption isotherms of DCF on RT-iCOF Langmuir model (Li et al. 2023a). Reproduced with permission. License number 5866430164899

(Alsudairy et al. 2023). Besides, Wei et al. (Wei et al. 2015) synthesised a two-dimensional enamine-linked COF utilising a quick microwave-assisted solvothermal technique in much less time and with a high yield at a low temperature. This iCOF was discovered to exhibit a high crystallinity, high stability, a large BET surface area, a high CO<sub>2</sub> capacity, and adsorption selectivity for CO<sub>2</sub>/N<sub>2</sub> (Wei et al. 2015).

### Room-temperature synthesis of iCOFs

Room-temperature synthesis approaches involve the creation of COFs at ambient temperatures (Maleki et al. 2024), usually by kinetically regulated reactions such as imine generation or click reactions (Li et al. 2019). This approach is useful for fragile building blocks or functional groups that might deteriorate in strong reaction conditions. ICOFs are good adsorbents for pollutant removal due to their unique structure and characteristics; however, standard iCOF synthesis is restricted by high temperatures and extended reaction times. Li et al. (Li et al. 2023a) presented the first room-temperature approach for synthesising iCOFs in 24 h (Fig. 5I). The room-temperature synthesised iCOF (RTiCOF) had higher crystallinity, a larger uptake capacity, and quicker kinetics than those synthesised at high temperatures



Fig. 6 Schematic illustration of the fabrication process and chemical structure of TpOMe-Pa-SO3H membrane (Fan et al. 2023). Reproduced with permission. License number 5866831293154

with extended reaction times. The adsorption kinetics, isotherms, and thermodynamics, as well as the impacts of ionic strength, pH, humic acid, and RT-iCOF reusability for diclofenac sodium, were thoroughly investigated (Fig. 5I). The produced RT-iCOF had the greatest adsorption capability and diclofenac sodium uptake capacity (Li et al. 2023a).

The morphology of COFs is an important aspect in determining their unique features. Chen et al. (Yu et al. 2023) synthesised a hollow COF with a flower-like structure (HFH-COF) at ambient temperature. The synthesised HFH-COF exhibits a large specific surface area, a mesoporous structure, high chemical stability, and good crystallinity. The unique shape of HFH-COF enabled high specific surface area utilisation and a quick mass transfer rate, resulting in a shorter equilibration time and improved extraction efficiency than spherical COF (S-COF) (Yu et al. 2023). Also, the complexity of biological materials makes it difficult to develop a simple, highly selective, and sensitive analytical approach for phthalate monoesters (mPAEs). Dan et al. (Dan et al. 2023) developed Cu<sup>2+</sup> immobilised magnetic COFs (Fe<sub>3</sub>O<sub>4</sub>@TtDt@Cu<sup>2+</sup> composites) with core-shell structures to improve the enrichment efficiency of mPAEs through a simple approach of synthesis of COF shells with inherent bifunctional groups on  $Fe_3O_4$  NPs and further  $Cu^{2+}$  immobilisation. The composites had a large specific surface area, strong saturation magnetisation, an ordered mesoporous structure,  $Cu^{2+}$  immobilisation, and exceptional thermal stability (Dan et al. 2023).

### Solid-state synthesis of iCOFs

Without the need for a solvent, iCOFs are directly formed from solid-state precursors in solid-state synthesis (Wei et al. 2024). To encourage the creation of covalent bonds and the development of crystalline COF structures, the precursors are combined and heated. This process can be both ecologically benign and useful for large-scale manufacturing. Fan et al. (Fan et al. 2023) developed a straightforward, scalable, and sustainable approach for creating iCOF membranes via solid-state synthesis based on mechanochemistry (Fig. 6). Time-dependent investigations show that the creation of the iCOF membrane involves both a morphological transition to a dense structure created by the restacking of nanosheet-like



Fig. 7 Schematic illustration of the preparation of EB-TFP and the "tandem post-synthetic modifications" (Li et al. 2023b). Reproduced with permission. License number 5866821258918

crystallites and a structural transformation from chaos to order. Because of the one-dimensional channels' plentiful proton-conducting sites and stiff crystalline framework structure, the resulting free-standing iCOF membranes exhibit excellent ion exchange capacity, mechanical strength, and similar proton conductivity (Fan et al. 2023).

### Post-synthetic modification of iCOFs

ICOFs can be customised by including a variety of platform functions (Rejali et al. 2023). Indeed, functioning is critical in their many applications. However, functional groups are not always compatible with reaction conditions, and they might compete with and interact with other monomer groups in the direct synthesis process (Ben et al. 2024a). In addition, the pre-synthesis of bulky moieties in COFs can have a deleterious effect on crystal formation. A post-synthetic alteration method can help prevent these issues. Furthermore, using this method, porosity size may be adjusted and stability enhanced without significantly affecting the crystallite. Besides, conductivity, hydrophobicity/hydrophilicity (Park et al. 2020), and chirality are among the properties that may be altered with this approach (Ben et al. 2024a; Segura et al. 2019). An anionic carboxylate ligand was used as a "molecular bridge" in Li et al. (Li et al. 2023b) global "tandem post-synthetic modifications" technique, which combines lanthanide ions with cationic COFs. Through ion exchange, an anionic carboxylate ligand was first added to cationic COFs. In the second step, the ligand was bound to Eu<sup>3+</sup> ions. In this case, 2.2-biquinoline-4.4-dicarboxylic acid disodium (BCA) was used to successfully introduce Eu<sup>3+</sup> to EB-TFP and confirm the viability of this technique, creating the hybrid system Eu<sup>3+</sup>@BCA@EB-TFP (Fig. 7). Besides, for the first time, Ren et al. (Ren and Geng 2024) constructed two cationic flexible COFs (iCOFs-AB-1 and iCOFs-AB-2) using a post-functionalisation procedure. At 77 °C, the I2 absorption capacities of the iCOFs-AB-1 and iCOFs-AB-2 are 3.36 and 4.26 g  $g^{-1}$  respectively, which is 1.19 and 1.14 times higher than those of neutral flexible COFs (Ren and Geng 2024). Furthermore, the safe disposal of radioactive materials, particularly nuclear waste containing iodine, has gained significant attention in the light of the advancements in nuclear energy. Therefore, a general method for post-synthetically modifying a hydroxy-functionalised COF (TAPT-COF-OH) to produce a cationic COF (TAPT-COF-AB) with a considerable amount of free bromide ions and investigating the iCOFs for iodine adsorption is described by Qi et al. (Mo et al. 2022). With a maximum adsorption capacity of up to 5.05 g g<sup>-1</sup>, TAPT-COF-AB has exceptional iodine adsorption capacity due to its wide BET surface area and superior crystallinity.

Moreover, post-synthesis modification techniques allow access to functionality that de novo syntheses cannot directly add to iCOFs (Segura et al. 2019). Currently used methods



Fig. 8 Schematic illustration of in situ synthesis of a spherical covalent organic framework as a stationary phase for capillary electrochromatography (He et al. 2022a). Reproduced with permission. License under CC-BY-NC-ND 4.0

for post-synthetic modification of iCOFs are utilising coordination chemistry to incorporate a range of active metal species, forming covalent bonds between incoming constituents and existing pendant groups, chemically converting linkages, monomer truncation technique can occasionally help with the post-synthetic modification by facilitating the internal functionalisation of COFs (Sun et al. 2022) and beyond post-synthetic modification, even more fascinating techniques are referred to as building block exchange (BBE), which includes framework-to-framework alterations that make use of the reversible bond creation that is a hallmark of COFs (Ben et al. 2024a). With the help of this tactic, it is possible to create new COF structures with entirely new components by using parent COF structures as templates to create protoCOF structures.

### **Amine-functionalised COFs**

A type of porous, crystalline material known as aminefunctionalised COFs are made of organic building blocks with amine functional groups integrated into their structures (Dautzenberg et al. 2023). Due to their special qualities and prospective uses in some industries, including adsorption, medication delivery, gas storage and separation, and catalysis, these materials have drawn a lot of interest (Tang et al. 2023). COFs functionalised with amino acids usually have organised structures, adjustable pore diameters, and large surface areas. A unique combination of chemical and physical characteristics, including greater hydrophilicity, enhanced interactions with guest molecules, and improved chemical stability, can be obtained when amine groups are present (Dautzenberg et al. 2023; Song et al. 2022).

Different bottom-up methods, such as solvothermal synthesis, microwave-assisted synthesis, and room-temperature synthesis, can be used to create amine-functionalised COFs (Du et al. 2015). The goal characteristics, amine content, and intended COF structure all influence the synthesis technique selection. The in situ synthesis method is the most widely used technique for creating amine-functionalised COFs (Grunenberg et al. 2021). This approach involves adding amine groups to the COF structure during the synthesis process itself, as opposed to adding them afterwards through post-synthetic modification. For a variety of chemical transformations, including oxidation processes, aldol condensation, and Knoevenagel condensation, amino-functionalised COFs can work as heterogeneous catalysts (Ji et al. 2018). Because of their robust adsorption capacities, these COFs have demonstrated encouraging promise for the removal of contaminants from water, including heavy metals, dyes, and PFASs (Ross et al. 2018).

### In situ synthesis of amine-functionalised COFs

A flexible technique for creating amine-functionalised COFs is in situ synthesis. With this method, amine functionalities are directly incorporated into the COF structure during synthesis, providing many benefits over post-synthetic alteration techniques (He et al. 2022a). For capillary electrochromatography separation, He et al. (He et al. 2022a) created a new spherical COF 1,3,5-tris(4-aminophenyl) benzene (TAPB) and 2,5-bis(2-propyn-1-yloxy)-1,4-benzenedicarboxaldehyde (BPTA) as an electrochromatography stationary phase (Fig. 8). A simple in situ growing technique was used to create the COF TAPB-BPTA modified capillary column at room temperature. The constructed column performed exceptionally well in the separation of chemicals such as phenols, chlorobenzenes, and alkylbenzenes (He et al. 2022a). Furthermore, the amino-carrying core-shell structured COFs nanospheres (Fe<sub>3</sub>O<sub>4</sub>@TpBD (NH<sub>2</sub>)<sub>2</sub>) were created by Wang et al. (Wang et al. 2020). Additionally, by post-synthetically modifying the  $(Fe_3O_4@TpBD(NH_2)_2)$ with 2-formylphenylboronic acid, a new magnetic boronate affinity adsorbent was created. With a quick magnetic response and a high binding capacity of up to 1037  $\mu$ mol g<sup>-1</sup>

for dopamine, the magnetic boronate affinity adsorbent is very effective. Additionally, it was employed as an adsorbent at neutral pH to extract urinary monoamine neurotransmitters (Wang et al. 2020).

The direct synthesis of COFs with specific amine characteristics and content is made possible by the in situ synthesis of amine-functionalised COFs. This can be useful for several applications, including drug administration, gas adsorption and separation, catalysis, and sensing. To get the required characteristics and functionality in the final aminefunctionalised COFs, however, meticulous optimisation of the reaction conditions and building block design could be necessary.

### **Porphyrin-based COFs**

A family of porous, crystalline materials known as porphyrin-based COFs is made up of porphyrin building blocks



**Fig.9** A schematic illustration of a condensation process between **a** para-phenylenediamine (PD) and meso-tetrakis (p-carboxyphenyl) porphyrin (TCPP) for the **b** effective absorption of methylene blue

(MB) (Wu et al. 2023). Reproduced with permission. License number 5867420914350

joined by covalent bonds (Zhao et al. 2024). Large, heterocyclic, aromatic molecules known as porphyrins have special optical, electrical, and biological qualities that make them appealing for a variety of uses (Zhao et al. 2024; Li et al. 2024b). Porphyrin building blocks can be joined into an ordered, extended framework by porphyrin-based COFs by a variety of condensation processes (Cao et al. 2024), including Schiff base condensation (Jiang et al. 2024) and transition metal-catalyzed coupling reactions (Shan et al. 2024). Usually, they have well-organised, porous structures with adjustable pore diameters and large surface areas. Porphyrin units can provide special qualities to the COF structure, such as the ability to capture light, redox activity, and metal coordination sites, which are helpful in a variety of applications (Jiang et al. 2024; Shan et al. 2024).

For light-driven processes such as singlet oxygen production, water splitting, and organic transformations, porphyrin-based COFs can function as photocatalysts (Issaka et al. 2022). Porphyrin-based COFs are suited for gas storage and separation applications, including CO2 capture and hydrogen storage, due to their porous nature (Issaka et al. 2023). Porphyrin-based COFs can be engineered to take advantage of their light-responsiveness and biocompatibility for imaging or drug delivery applications (Issaka and Amu-Darko 2024). All things considered, porphyrin-based COFs are promising materials for a variety of applications in catalysis, energy, sensing, and biomedicine because they combine the structural benefits of COFs with the special qualities of porphyrins. Realising their full potential will require more study on the optimisation of their synthesis, structure, and characteristics.

### Condensation reaction for synthesising porphyrin-based COFs

Several condensation reactions can be used to create covalent bonds between porphyrin building blocks and linkers to synthesise porphyrin-based COFs (Chen et al. 2021). For example, in Schiff base condensation, an amine group and an aldehyde group combine to form a C = N bond; in Aldolammonia condensation, an aldehyde group reacts with an amino group and a second aldehyde group to form a new C–C bond and a C = N bond; and A boronic acid group from the porphyrin or linker reacts with a diol or polyol from the porphyrin or linker to produce boron-oxygen-carbon (B-O-C) bonds in a process known as boronic acid condensation (Das et al. 2024). Besides, by using metal-catalyzed coupling processes, porphyrin building blocks and linkers can generate covalent connections (Sonogashira or Suzuki coupling, for example) (Wu et al. 2023).

However, Schiff base condensation is a widely used technique because of its adaptability and ease of use in the construction of COFs (Jiang et al. 2024). The 2D porphyrin-based covalent organic framework (Por-PD-COF) with amide linkages was created and synthesised by Wu et al. via a condensation process between para-phenylenediamine (PD) and meso-tetrakis (p-carboxyphenyl) porphyrin (TCPP) (Fig. 9a). Por-PD-COF's large surface area, plenty of active sites, and strong stability allow it to swiftly and effectively absorb methylene blue (MB) and extract it from aqueous solution (Fig. 9b). Furthermore, Oudi et al. (Oudi et al. 2023) created and synthesised the material via a solvothermal condensation reaction between 1,4-benzene boronic acid (DBBA) and 5,10,15,20-tetrakis-(3,4-dihydroxyphenyl) porphyrin (DHPP). Under visible LED light irradiation, the resulting multifunctional COF demonstrated exceptional performance in catalysing a one-pot tandem selective benzylic C-H photooxygenation/Knoevenagel condensation process without the need for additives or metals. Notably, the COF remained stable and reusable for four consecutive cycles, and its catalytic activity was higher than that of its organic equivalents (Oudi et al. 2023).

By meticulously picking appropriate porphyrin building blocks and linkers and optimising the reaction conditions, these condensation processes may be used to synthesise porphyrin-based COFs with desired architectures and characteristics. The required COF structure, porosity, and stability, as well as the availability and convenience of handling the starting components, all influence the synthesis process used.

### Hydrophobic COFs

Hydrophobic COFs are a family of crystalline, porous materials with a strong aversion to water (Li et al. 2022). They are made of organic building pieces joined by covalent connections. These COFs' hydrophobic properties result from the orderly organisation of their porous structures and the presence of nonpolar or low-polarity functional groups (Li et al. 2022; Deng et al. 2022). Building blocks having hydrophobic properties can be used to create hydrophobic COFs, and their creation can be enhanced by adjusting reaction conditions. For particular purposes, the pore diameters, surface areas, and chemical capabilities of hydrophobic COFs may be precisely engineered. Nonpolar organic molecules can be selectively adsorbed to and separated from aqueous solutions using hydrophobic COFs (Zhang et al. 2024a). Because of their hydrophobic qualities, which encourage the preferential adsorption of hydrophobic molecules, organic contaminants or important compounds may be effectively separated from water. Through modifications to their optical, electrical, or magnetic characteristics, hydrophobic COFs can be used for the selective sensing and detection of hydrophobic analytes, such as organic vapours or dissolved molecules (Song and Kang 2023). All things considered, hydrophobic COFs provide special qualities and chances for



**Fig. 10** Schematic illustration of the **a** synthesis of imine-linked COFs in aqueous solution. **b** the formation process of imine through nucleophilic addition of amine on acid-preactivated aldehyde (Kong et al. 2024). Reproduced with permission. License under CC-BY-NC-ND 4.0

a range of uses, including medication distribution, sorption and separation, catalysis, and sensing. To the fullest extent possible in various domains, these materials must be developed and optimised.

# Schiff base condensation for the synthesis of hydrophobic COFs

Schiff base condensation is the most widely used technique for creating hydrophobic COFs (Ajmal et al. 2024). An amine group from one building block and an aldehyde group from another building block combine to generate a C = Nbond during this reaction. Because Schiff base condensation is so easy to utilise, versatile, and produces strong, porous frameworks (AlNeyadi et al. 2024), it is frequently employed for COF synthesis. For Schiff base condensation processes and the synthesis of imine-linked COFs, acid catalysts are essential. In Schiff base condensations, the amine attacks the aldehyde nucleophilically to create an intermediate hemiaminal (Jiang et al. 2024), which is then dehydrated to generate the imine.

Typically, solvothermal conditions call for the use of hazardous organic solvents, high reaction temperatures, and intricate procedures are used to synthesise COFs. Their infusibility and insolubility also provide significant processing issues for COFs. A simple, environmentally friendly method for producing imine-linked COFs at room temperature in an aqueous solution was described by Kong et al.

(Kong et al. 2024). The control of the reaction rate is the secret to the synthesis (Fig. 10a). Acetic acid pre-activation greatly increases the reactivity of aldehyde monomers in aqueous solutions. In contrast to traditional solvothermal synthesis, the still-somewhat-lower imine creation rate and greater imine breakdown rates in aqueous solution enable the modification of the reaction equilibrium and the crystallisation of the products. Thus, in a matter of minutes, highly crystalline COFs with sizable surface areas may be produced in reasonably high yields (Fig. 10b). The adaptability of this technique is demonstrated by the effective synthesis of 16 COFs from monomers with varying molecular sizes, geometries, pendant groups, and core structures (Kong et al. 2024). Besides, Bügel et al. (Bügel et al. 2022) synthesised two imine-linked COFs via a catalyst-free Schiff base reaction. HHU-COF-1 was created via the condensation reaction of 1,3,5-tris-(4-aminophenyl)triazine (TAPT) with 4,4'-biphenyldicarboxaldehyde. With the help of 2,2',3,3',5,5',6,6'-octafluoro-4,4'-biphenyldicarboxaldehyde, the fluorinated analogue HHU-COF-2 was produced. The polymer Matrimid was utilised to create mixed-matrix membranes (MMMs) using the by-products of a larger-scale synthesis (Bügel et al. 2022).

Hydrophobic COFs are synthesised and customised for a range of uses, including selective adsorption and separation, catalysis, drug administration, and sensing, by using Schiff base condensation and carefully choosing hydrophobic building blocks.

# Advantages of covalent organic frameworks (COFs) for PFAS absorption

COFs, like metal-organic frameworks (MOFs), and zeolites, are crystalline (Singh et al. 2025), porous, and organic structures with atoms joined by covalent bonds (Nazir et al. 2024). COF crystallinity is determined by the proper design of the organic building blocks. During crystallisation, reversible bond creation provides error correction (Mushtaq et al. 2024). Furthermore, the reticular structures of COFs are formed by linking different symmetric monomers resulting in distinct structures (Li et al. 2025). Despite their vulnerability in aquatic environments, COFs have demonstrated great stability and stiffness under temperature conditions. COFs also have a homogeneous nanopore network structure with a large specific surface area (Zhu et al. 2023). Despite their similarity in crystallinity and porosity, COFs offer numerous benefits over other porous materials, such as zeolites and MOFs, when utilised as adsorbents for PFAS in water: One key advantage is the ability to tailor pore size and functioning (Hao et al. 2024). COFs are synthesised with precise control over pore size, structure, and functionality, enabling the development of materials with optimal PFAS adsorption characteristics. Wang et al. (Wang et al. 2024c) synthesised COFs with five different pore sizes (COF1-COF5) and used kinetic models to perform a thorough investigation. Their findings showed that the adsorption capacity and rate of methyl orange (MO) increased linearly with COF pore size from 1.25 to 2.57 nm. COF3, having a pore size of 2.57 nm, had the best adsorption capability for MO, with an outstanding capacity of 43.07 mg  $g^{-1}$ . Furthermore, Liu et al. (Liu et al. 2023b) revealed that a novel type of MOFfunctionalised COFs with a large surface area, numerous binding sites, and outstanding chemical and structural stability were synthesised to improve structure stability and selective recognition efficiency. COFs are considerably beneficial over zeolites and MOFs and can be used to functionalize such adsorbents to enhance pore diameters and restrict functionalisation choices.

Besides, COFs have high chemical stability in aqueous settings, which is critical for PFAS adsorption applications. In contrast, zeolites can degrade in acidic or alkaline settings, whereas MOFs may experience metal leaching and structural collapse in water (Zhang et al. 2024b). Zhang et al. (Zhang et al. 2025) used a solvothermal technique to synthesise guanidine-linked COF. The inclusion of guanidine groups in its structure improved electrostatic interactions and supplied hydrogen bonding sites, allowing for the selective adsorption of PFCAs from ambient water samples. Furthermore, guanidine-linked COF showed various advantages, including strong selectivity for PFCAs, high adsorption capacity (2005 mg g<sup>-1</sup>), outstanding chemical stability, and impressive recyclability (five cycles). Furthermore, COFs

are naturally hydrophobic due to their primarily hydrocarbon-based makeup (Lan et al. 2024a), which increases their affinity for PFAS chemicals while reducing water adsorption (Karbassiyazdi et al. 2023). This feature can enhance PFAS removal efficiency and adsorption capacity when compared to more hydrophilic materials like zeolites and MOFs (Peng et al. 2025). The good hydrophobic trifluoromethyl-enriched COF was devised and synthesised as a covering for solid-phase microextraction (SPME) by Lan et al. (Lan et al. 2024b). The hydrophobic trifluoromethylenriched COF's strong adsorption selectivity for Polycyclic aromatic hydrocarbons (PAHs) is due to interactions with PAHs like hydrophobicity,  $\pi$ - $\pi$ , and H bond interactions. The suggested technique produced quick adsorption of PAHs and reduced the adsorption equilibrium period to 15 min. Using gas chromatography-tandem mass spectrometry (GC-MS/ MS), PAHs were found in the range of 0.008–0.16 ng mL<sup>-1</sup>, with a quantitative limit of 0.029-0.47 ng mL<sup>-1</sup>.

COFs can be easily regenerated and reused for several adsorption-desorption cycles with no loss of performance (Emmanuel et al. 2024). This is a significant benefit over zeolites and MOFs, which may need severe regeneration conditions or have lower adsorption capability during regeneration. Zhang et al. (Zhang et al. 2024c) used a reasonable strategy to create a hydrogel composite material by encapsulating NH<sub>2</sub>-MIL-101(Cr)/COFs in sodium alginate (SA), which efficiently captures tetracycline (TC). The as-prepared composite displayed outstanding TC adsorption capabilities, with a clearance rate of 96.38% in 120 min. The adsorbent also showed exceptional recyclability, with just a little loss in removal efficiency (85.5% and 142 mg  $g^{-1}$ ) after ten cycles of adsorption and regeneration. Moreover, COFs are often made up of non-toxic organic building blocks (Manzoor et al. 2024), making them more ecologically benign than MOFs, which frequently include metal ions that might pose environmental and health hazards when degraded or leached. Li et al. (Li et al. 2021) employed a commercial, low-toxicity hydrazide-containing building block to synthesise azine-linked COFs. Flexible formic hydrazide (FH) was combined with 1,3,5-triformylphloroglucinal (Tp) or 1,3,5-triformylbenzene (TFB) to create new-style COFs. The two resultant COFs (TpFH and TFBFH) had a consistent hollow tubular shape composed of amine and aldehyde groups. The breakdown of FH slows down the reaction rate, and the as-synthesised FH-series COFs (708 m<sup>2</sup> g<sup>-1</sup> for TpFH and 888 m<sup>2</sup> g<sup>-1</sup> for TFBFH) have larger specific surface area than hydrazine-series COFs (617 m<sup>2</sup> g<sup>-1</sup> for TpAzine and 472  $m^2 g^{-1}$  for TFBAzine).

COFs have several benefits over other porous materials for PFAS adsorption in water. These intriguing qualities have great potential for further development of efficient and sustainable PFAS removal solutions.

### **Properties of various COFs for PFAS adsorption**

### Properties of ionic COFs for PFAS adsorption

ICOFs have demonstrated encouraging properties for the adsorption of pervasive and harmful substances, PFASs. Different ionic functional groups, including quaternary ammonium salts, can be included in iCOF designs to interact electrostatically with PFASs and facilitate effective adsorption (Zhang et al. 2021). ICOFs' porous structure increases the surface area and number of adsorption sites available for PFASs, hence improving their adsorption ability. For certain PFASs, the pore size can be adjusted to maximise the adsorption efficiency. Owing to this knowledge, Tang et al. (Tang et al. 2022) synthesised a stable and well-compatible cationic based on the structure of three PFASs (perfluorobutylenesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), and perfluorooctylsulfonic acid (PFOS)) and a medium's property. Analytes were detected and adsorbed using matrix-assisted laser desorption/ionisation time-offlight mass spectrometry (MALDI-TOF MS) using the prepared framework as an adsorbent. The C-COFs' structural characteristics were described. To get the optimum enrichment efficiency, enrichment parameters such as the type and volume of dispersion solution, pH, adsorbent quantity, and enrichment duration were optimised (Tang et al. 2022). Furthermore, in addition to electrostatic interactions, iCOFs frequently have hydrophobic channels that aid in the adsorption of PFASs through hydrophobic interactions (Sun et al. 2022). The ability to synthesise iCOFs with high crystallinity and regulated size enhances their adsorption capacity and facilitates their easy separation from the treated water following the elimination of PFASs. They may also be used again for PFAS adsorption because of their strong chemical and thermal durability.

In general, the large surface area, porosity, hydrophobic channels, controllable size, stability, reusability, and adjustable ionic functionality of iCOFs make them materials that show promise for the effective removal of PFASs from polluted water. It is necessary to conduct more study on the optimisation of iCOFs and their real-world use in PFAS cleanup.

### Properties of β-CD-COFs for PFAS adsorption

Promising qualities have been shown by  $\beta$ -CD-COFs for the adsorption of PFASs (Wang et al. 2021a). Through host–guest chemistry and hydrophobic interactions,  $\beta$ -CD molecules can form inclusion complexes with PFASs, therefore improving their adsorption. Three distinct  $\beta$ -CD adsorbents were evaluated by Abaie et al. (Abaie et al. 2024) for their ability to remove a combination of PFASs at neutral pH, including anionic, neutral, and zwitterionic compounds. To measure each PFAS's adsorption affinity, the researchers computed linear partition coefficient (K<sub>d</sub>) values.  $\beta$ -CD polymers that were crosslinked with epichlorohydrin ( $\beta$ -CD-EPI) and hexamethylene diisocyanate ( $\beta$ -CD-HDI) showed some PFAS adsorption. *N*-dimethyl amonia propyl perfluorohexane sulfonamide (AmPr-FHxSA) was eliminated by  $\beta$ -CD-EPI and  $\beta$ -CD-HDI, whereas  $\beta$ -CD-Cl showed no affinity for zwitterionic compounds (Abaie et al. 2024).

Furthermore, for PFASs,  $\beta$ -CD-COFs show quick adsorption kinetics, achieving adsorption equilibrium in a matter of minutes (Sahu et al. 2023). Their organised pores and the special structure of  $\beta$ -CD are responsible for this fast adsorption.  $\beta$ -CD-COFs have superior PFAS adsorption capabilities compared to conventional adsorbents such as resins and activated carbons. Their porous structure and the unique interactions between  $\beta$ -CD and PFASs are responsible for their high capacity (Abaie et al. 2024). Because of the great selectivity of  $\beta$ -CD-COFs for PFASs, these pollutants may be effectively removed from water even when other compounds are present. Moreover,  $\beta$ -CD-COFs have strong thermal and chemical durability, which makes it possible to employ them again for PFAS adsorption. Owing to these qualities,  $\beta$ -CD-COFs are materials that show great promise for effectively removing PFASs from polluted water. It is necessary to do more study on the optimisation of  $\beta$ -CD-COFs and their practical use in PFAS cleanup.

## Properties of amine-functionalised COFs for PFAS adsorption

Due to the porous structure and the potent interactions between amine groups and PFASs, amine-functionalised COFs exhibit high adsorption capacities for PFASs (Ateia et al. 2019a). The positive charge of the amine groups in COFs allows them to interact electrostatically with the negatively charged PFASs. Additionally, they exhibit strong PFAS selectivity, making it possible to effectively remove these pollutants from water even when other compounds are present. Ji et al. (Ji et al. 2018) demonstrated that at concentrations relevant to the environment, imine-linked twodimensional (2D) COFs containing primary amines readily adsorb ammonium perfluoro(2-methyl-3-oxahexanoic) acid (GenX). The greatest capacity and quickest removal were demonstrated by COFs with partial amine incorporation, indicating that the synergistic interaction of the hydrophobic surface and the polar group is what causes GenX binding. More than 90% of the 12 out of 13 PFAS were also eliminated by a COF with a 28% amine loading. These findings highlight the potential of COFs in the removal of PFAS and offer design guidelines for optimising adsorbent efficiency (Ji et al. 2018).

Additionally, the high chemical and thermal durability of amine-functionalised COFs makes them suitable for recurrent usage in the adsorption of PFASs (Song et al. 2022). By modifying the synthesis conditions or precursor selection, the amine concentration in COFs may be regulated, enabling the COF's adsorption ability for particular PFASs to be optimised. Owing to these qualities, amine-functionalised COFs hold great promise as materials for effectively removing PFASs from polluted water. It is necessary to do more studies on the practical application of amine-functionalised COFs in PFAS cleanup as well as their optimisation.

### Properties of porphyrin-based COFs for PFAS adsorption

Porphyrin-based COFs have high specific surface areas and variable porosity, allowing for effective PFAS adsorption due to the vast number of accessible adsorption sites (Asayesh-Ardakani et al. 2024). The hydrophilic characteristic of porphyrin-based COFs can aid in the adsorption of PFASs by increasing contact between the COF surface and the molecules. Furthermore, high surface wettability can aid in the migration of PFASs into COF pores. Qian et al. (Qian et al. 2024) reported the synthesis of Por-MA, a photothermal porphyrin-based COF for the effective removal of PFASs from environmental water. Por-MA's crystalline structure, rich in nitrogen, allows for electrostatic and hydrogen bonding interactions for PFAS adsorption. It had a high adsorption capacity (686.6 mg g<sup>-1</sup>) and rapid kinetics (equilibrium time < 10 min) for perfluorooctanoic acid (PFOA) at 25 °C, outperforming other COF-based sorbents.

Porphyrin-based COFs' structure and functional groups may be altered, which enables the adsorption performance of these molecules to be optimised for certain PFASs. To improve interactions with target PFASs, it is possible to customise pore diameters, pore functionality, and surface chemistry. Owing to these properties, Xie et al. (Xie et al. 2023) created ordered crystalline COFs by using calix[4]arene (CX4) as a building component. The ideal fusion of COFs' porosity and CX4's host-guest recognition ability results in the CX4-COFs' selective and potent adsorption capability for linear molecule PFASs (261-1055). PFASs in food were then found using the CX4-COFs as adsorbents. The technique demonstrated high accuracy (1.3-9.8%) and low detection limits  $(0.11-0.28 \text{ ng kg}^{-1})$  when used to simultaneously enrich and determine six PFASs in fish, prawns, and shellfish. Satisfactory recoveries (79.9-118%) were achieved (Xie et al. 2023). A few COFs based on porphyrins have photothermal characteristics that can be used to adsorb and



Fig. 11 Fluorinated quaternary ammonium COFs: a schematic representation for the effective and selective removal of common per- and polyfluoroalkyl compounds (Wang et al. 2023b). Reproduced with permission. License number 5755691103588

degrade PFASs. These COFs can produce localised heat in response to light irradiation, which facilitates PFAS diffusion and adsorption within the porous structure (Gharanli et al. 2024). Furthermore, the breakdown of PFASs that have been adsorbed can be aided by the photothermal effect, which might enhance the remediation process as a whole (Qian et al. 2024). Because of their strong chemical and thermal stability, porphyrin-based COFs may be used repeatedly for the adsorption of PFASs. Concerning PFAS adsorption, porphyrin-based COFs have favourable characteristics such as large surface areas, adjustable architectures, and photothermal capabilities. It is necessary to conduct more study on the development of porphyrin-based COFs and their actual use in PFAS cleanup.

### Properties of hydrophobic COFs for PFAS adsorption

Numerous characteristics of hydrophobic COFs make them attractive materials for PFAS adsorption. Because of their structured porosity architectures and nonpolar or lowpolarity functional groups (Ajmal et al. 2024), hydrophobic COFs have excellent water-repelling qualities. The ability of hydrophobic perfluoroalkyl substances (PFASs) to selectively adsorb onto water molecules amplifies the effectiveness of PFAS removal from polluted water sources. With their high specific surface areas and adjustable porosity, hydrophobic COFs offer plenty of PFAS adsorption sites. These characteristics help to increase the efficiency and capacity of adsorption (Gharanli et al. 2024). A novel hydrophobic COF that exhibits high PFAS adsorption affinity. The condensation reaction of 2,4,6-trimethyl-1,3,5-triazine with 2,3-dimethoxyterephthaldehyde produced COF-I, which was thoroughly characterised and shown high crystallinity and surface area as well as strong hydrolytic and thermal stability (Zarei et al. 2024).

Because of their strong chemical and thermal durability, hydrophobic COFs may be used repeatedly for the adsorption of PFASs (Xing et al. 2020). A variety of processes, including hydrophobic interactions,  $\pi$ - $\pi$  stacking, electrostatic interactions, and van der Waals forces, can be used by hydrophobic COFs to adsorb PFASs (Zarei et al. 2024). When designing COFs for improved PFAS adsorption, an understanding of these processes might be helpful. All things considered, hydrophobic COFs have attractive qualities for PFAS adsorption, such as hydrophobicity, large surface areas, stability, and adjustable architectures. It is necessary to do more study on how to best use these qualities and apply them practically in the remediation of PFASs.

### Applications of COFs as an adsorbent for PFAS remediation

To specifically adsorb PFASs from polluted water sources, COFs can be engineered with certain pore diameters and surface functions. Particularly  $\beta$ -CD, amine-functionalised, porphyrin-based, ionic, and hydrophobic COFs have a high affinity for PFASs, which makes it possible for these persistent pollutants to be effectively adsorbed and removed (Table 2). In addition to COFs showing excellent extraction efficiency (Hou et al. 2020b), they also show excellent selectivity for PFASs (Sun et al. 2021). Besides, negatively charged PFAS and positively charged COFs interact electrostatically (Li et al. 2023c). Functional groups like carboxylate ion (COO<sup>-</sup>) or sulphur trioxide ion  $(SO_3^{-})$  (Björneholm et al. 2022) that give a molecule a negative charge under neutral pH circumstances are commonly found in PFAS compounds (Li et al. 2023c; Björneholm et al. 2022). Adsorption or binding of PFAS onto the COF surface can occur when positively charged COFs are present because of the electrostatic interaction between the positively charged sites on the COFs and the negatively charged functional groups on PFAS molecules (Ji et al. 2018).

Wang et al. (Wang et al. 2023b) created unique COFs with strong adsorption selectivity and capacity for PFAS by combining mixed edges in their structural design (Fig. 11). To make optimal fluorinated quaternary ammonium COFs, the COFs were created with the proper pore size. The edge of the COFs was replaced with varied ratios of fluorinated edge and quaternary ammonium edge. The COFs that were synthesised had a very consistent adsorption performance across a range of solution pH, ionic strength, and humic acid concentrations. For PFHxS and PFOS, they demonstrated a high adsorption capacity of 300.2 and 879.8 µmol/g, respectively. More importantly, compared to powdered activated carbon and anion exchange resins, fluorinated quaternary ammonium COFs can effectively remove multiple PFAS from actual electroplating wastewater simultaneously and selectively adsorb PFAS in the presence of different hydrocarbons with similar structures. The C-F chain on COFs effectively adsorbed the PFAS, but the C-H chain of hydrocarbons was repelled by the C-F chain, according to density functional theory (DFT) calculations. In addition, the COFs demonstrated a reasonably steady adsorption capability for PFAS within 5 cycles and were well-regenerated by the combination of NaCl and methanol solution. These findings provide a different approach to bifunctional modification that can effectively and selectively eliminate PFAS from water (Wang et al. 2023b).

Additionally, hydrophobic interactions between the COF's pore walls and PFAS tails are dominated by fluorine (F) groups (Ateia et al. 2019b). The majority of the time,

Table 2 COFs techniques used to detect and quantify numerous PFAS types in a variety of samples

Type of PFAS	Sample extrac- tion method	COF framework	Sample detection technique	Recovery rates	LOD	Refs
GenX, PFOS, and PFOA	Magnetic SFE	Cationic- fluorinated (CF)-COF	LC–MS/MS	73.5–118%	0.003–0.019 ng g <sup>-1</sup>	Gong et al. (2024)
PFHxS and PFOS	LPE	Fluorinated quaternary ammonium COFs	LC- HPLC	PFOS = 24.7% PFHxS = 20.1%	PFHxS = 300.2 $\mu$ mol/g PFOS = 879.8 $\mu$ mol g <sup>-1</sup>	Wang et al. (2023b)
PFOS, and PFOA	SPME	Trifluorome- thyl covalent organic framework (CF <sub>3</sub> -COF)	UHPLC-MS/MS	91.0–110%	$0.1-0.7 \text{ pg g}^{-1}$	Sun et al. (2020)
PFOS, and PFOA	SPME	Triazine core-based F-functional- ised COFs	Nanoelectrospray ionization mass spectrometry (nanoESI-MS)	np	$0.02-0.8 \text{ ng } \text{L}^{-1}$	Hou et al. (2020a)
GenX	SPME	Dioxin-linked covalent organic frame- work (TH-CO)	UHPLC-MS/MS	89.5–105%	$0.0020-0.0045 \text{ ng L}^{-1}$	Ji et al. (2020)
PFOS, and PFOA	SPME	Cationic COF	LC-HPLC	GenX = 80% HFPO- TA = 100%	GenX = $2.06 \text{ mmol g}^{-1}$ HFPO- TA = $2.16 \text{ mmol g}^{-1}$	Wang et al. (2021b)
PFOS, and PFOA	SPME	Imprinted cova- lent organic frameworks (CMIP)	UHPLC-MS/MS	np	0.1–0.3 ng g <sup>-1</sup>	Zhang et al. (2024e)
PFOA	SPME	COF@ chitosan (COF@CS)	LC-HPLC	np	$2.8 \text{ mmol g}^{-1}$ at pH 5	Zhang et al. (2024d)
GenX, PFOS, and PFOA	SPME	Fluoro-function- alised/chitosan COF (chitosan/ F-COF)	LC-HPLC	88.4%	np	He et al. (2022b)
Six anionic PFAS	SPME	Viologen COF: MELEM-COF and MEL-COF	np	90.0–99.0%	2500 mg g <sup>-1</sup>	Zadehnazari et al. (2024)

hydrophobic and electrostatic interactions work together to adsorb PFAS (Ateia et al. 2019b; Thompson et al. 2024). Because PFSA is more hydrophobic than perfluorinated carboxylic acids with the same chain length (Sharma et al. 2024), amine group adsorbents have a greater affinity for PFAS (Sharma et al. 2024; Thompson et al. 2024). Furthermore, compared to shorter-chain PFAS, which depends on electrostatic interactions, long-chain PFAS is more easily absorbed (Zahmatkesh et al. 2024; Thompson et al. 2024). Gong et al. (Gong et al. 2024) created a cationic-fluorinated (CF)-COF by post-modification, which they then utilised as a magnetic solid-phase extraction adsorbent for the adsorption of PFASs. Eight long-chain PFASs in food were identified using a unique approach that combined CF-COF-based magnetic solid-phase extraction with LC-MS/MS. The approach demonstrated low detection limits of 0.003–0.019 ng  $g^{-1}$  and good recovery rates of 73.5–118% for PFASs under optimal circumstances. This work presents a new concept for the creation of PFAS-targeting adsorbents as well as a fresh analytical technique for PFAS in food monitoring (Gong et al. 2024). Furthermore, Sun et al. (Sun et al. 2020) have developed a simple room-temperature method for synthesising trifluoromethyl COF (CF<sub>3</sub>-COF) for solid-phase microextraction (SPME). When compared to commercially available SPME coating, non-contained fluorine COF coating, and amorphous polymer coating, the CF<sub>3</sub>-COF coating exhibits better extraction performance for PFASs. The density functional theory computation is used to show the trifluoromethyl's fluorine affinity for PFASs in CF<sub>3</sub>-COF. The targeted PFASs were micro-extracted using CF<sub>3</sub>-COF-coated fibre, eluted with 1 mL acetonitrile, and then quantified using

UHPLC-MS/MS. The excellent sensitivity is shown by the LODs, which are 0.1–0.7 pg  $g^{-1}$  for milk and 0.2–0.8 pg  $g^{-1}$ for milk powder. The method's accuracy is within the range of 2.9-9.9%. The repeatability from fibre to fibre ranges from 4.2 to 9.5%. The relative recoveries under ideal circumstances are 89.8 to 111% with RSDs < 10% for milk powder and 91.0–110% with RSDs  $\leq 10\%$  for milk (Sun et al. 2020). Besides, SPME and nanoelectrospray ionisation mass spectroscopy (nanoESI-MS) are two novel techniques that Hou et al. (Hou et al. 2020a) developed for the fast and ultrasensitive analysis of PFASs in biological and environmental samples. The F-functionalised COFs coating on the novel SPME probe allowed for highly selective enrichment of trace PFASs, and the extracted COFs-SPME probe was then loaded and applied directly to nanoESI-MS analysis in both ambient and open-air settings. For each of the fourteen PFASs in water that were studied, the technique demonstrated acceptable linearities between 1 and 5000 ng  $L^{-1}$  with correlation coefficient values of at least 0.9952. The ranges of the quantification and detection limits were 0.06–3 ng  $L^{-1}$  and 0.02–0.8 ng  $L^{-1}$ , respectively. The suggested technique was successful in achieving ultrasensitive PFAS detection in ambient water and whole blood (Hou et al. 2020a).

Moreover, He et al. (He et al. 2022b) created a unique COF and employed it as an effective adsorbent to remove PFASs from water. First, a room-temperature Schiff base reaction was used to create a fluoro-functionalised COF (F-COF). The surface of F-COF was subsequently changed by a layer of chitosan using a cross-linking polymerisation process. Concerning PFASs, the resulting chitosan/F-COF exhibits strong adsorption capability through electrostatic interaction, hydrogen bond interaction, fluorine-fluorine interaction, and channel size selection. It also had favourable hydrophilicity, surface wettability, and high specific surface area. Chitosan/F-COF was tested for its ability to adsorb GenX, PFOS, and PFOA. In samples of sewage and lake water, the chitosan/F-COF combination demonstrated a strong capacity for simultaneous absorption of PFASs, with removal efficiencies exceeding 88.4% for three of the PFASs (He et al. 2022b). Besides, through electrostatic interactions, a quaternary amine COF with a naturally occurring positive surface charge was created to adsorb PFOA by Zhang et al. (Zhang et al. 2024d). After that, a straightforward dissolution evaporation procedure was used to mix the COF with chitosan (CS) to create a composite gel substance known as COF@CS. The results showed that COF@CS's adsorption capability much outperformed that of the original COF and CS. The Langmuir model indicates that at pH 5, COF@ CS reached a maximum PFOA capacity of 2.8 mmol  $g^{-1}$ . Additionally, compared to 5.9 mmol g<sup>-1</sup> h<sup>-1</sup> for COF and 3.4 mmol  $g^{-1} h^{-1}$  for CS, the adsorption rate rose dramatically to 6.2 mmol  $g^{-1} h^{-1}$ . Notably, for eight more PFAS classes, COF@CS demonstrated exceptional removal effectiveness (Zhang et al. 2024d).

# Challenges and prospects of COFs for PFAS adsorption

Although COFs have a lot of potential for adsorbing PFASs from water, their actual use is fraught with difficulties. These difficulties might consist of the following:

### Synthesis scalability

Challenge The restricted scalability and fragility of COFs pose significant hurdles in their commercialisation and industrial applications. According to Vardhan et al. (Vardhan et al. 2023), stable dynamic linkage is required to connect building blocks in a network structure, which often requires closed conditions to ensure the reversibility of condensation processes. Furthermore, the current go-to techniques (solvothermal method) for synthesising COFs typically have low yields (Osman et al. 2024), meaning that only a tiny portion of the finished product can be made from the starting ingredients (Vardhan et al. 2023). Meanwhile, Xiao et al. (Xiao et al. 2023) found that typical solvothermal synthesis of COFs requires a long reaction time and a constant highenergy input to push the reaction equilibrium and yield thermodynamically stable crystallisation products. To address these issues and align with the current notion of energy saving, synthesis scalability, and emission reduction, several novel methodologies are required (Zhu et al. 2024). Segura et al. (Segura et al. 2016) also discussed the use of aqueous acetic acid (AcOH) as a catalyst in the 1,4-dioxane: mesitylene combination, which experienced the typical solvothermal reaction to carry out imine-based COF at 120 °C; the resultant powder was un-processable and unscalable. As a result, unique alternative synthetic processes are required to meet the limitations of typical conditions.

**Prospects** To enhance the scalability of COF production, researchers are looking at new synthesis techniques, substitute precursors, and more effective catalysts. As a result, numerous solutions have recently been developed to prevent reaction scenarios involving high pressure and temperature. The most notable include room temperature (Bagheri and Aramesh 2021), water (Martín-Illán et al. 2020), sonochemical synthesis (Zhao et al. 2022), and sol–gel synthesis (Zhu et al. 2021). Although these technologies save energy and money, they provide lower-quality crystalline samples (Martín-Illán et al. 2023). Nonetheless, they provide beneficial results. There is still increasing interest in creating COF synthesis processes that are sustainable, scalable, and environmentally benign. While various green alternatives including non-toxic organic solvents have been described

(Martín-Illán et al. 2020, 2023), there are few instances of energy-efficient and cost-effective technologies that do not use dangerous solvents. In the end, resolving the synthesis scalability issue is essential to maximising the promise of COFs as a suitable adsorbent for PFAS adsorption.

### Long-term stability and regeneration

Challenge With regards to PFAS removal from water environments via adsorption, the long-term stability and regeneration of COFs are critical aspects that dictate their practical application. Furthermore, these COFs should be able to withstand deterioration in a variety of chemical and environmental environments (Shah et al. 2023). For the efficient adsorption of PFAS from aqueous environments, COFs must resist hydrolysis, to avoid the weakening of its structural framework, thereby ensuring optimum adsorption capability. Furthermore, during adsorption, regeneration, or handling, COFs may be subjected to mechanical stressors like pressure or abrasion. In these situations, COFs must preserve their structural integrity. The COF structure shouldn't undergo permanent alterations as a result of high temperatures, which can occur during adsorption procedures or regeneration.

**Prospects** It is still difficult to create COFs that are crystalline, stable, and functional at the same time, as reversible bond formation is a necessary condition for COF crystallisation (Ghosh et al. 2024). However, as the COF field evolves, new techniques have emerged that avoid the crystallinitystability contradiction. Haase and Lotsch (Haase and Lotsch 2020) discussed three major approaches to obtaining both stable and crystalline COFs: adjusting the reaction conditions for reversible linkages, separating the order-inducing and stability-inducing steps, and controlling the structural degrees of freedom during assembly and in the final COF. This work paves the way for addressing these challenges, as the stability and regeneration of COFs can effectively facilitate the industrial removal of PFAS from water.

### Environmental compatibility and toxicity

**Challenge** For COFs to be used safely and sustainably in water treatment applications, such as PFAS adsorption, their toxicity and environmental compatibility are important factors to take into account. The ideal COFs would be biodegradable, which means they could organically decompose in the environment without endangering ecosystems. During their manufacture, usage, or destruction, COFs shouldn't release any hazardous materials into the environment, such as heavy metals or poisonous organic compounds (Shah et al. 2023; Vakili et al. 2024). Moreover, the adsorption efficacy of COF may be lowered by the buildup

of microbes on its surface. Further investigation is needed into the long-term harm caused by COFs and their breakdown products due to repeated exposure. Chronic toxicity, affecting growth, reproduction, and overall health, should be assessed through long-term studies. The accumulation of COFs and their breakdown products may negatively impact both individual organisms and the food chain. Evaluating the potential for bioaccumulation and biomagnification of COF-related chemicals in the environment is essential.

Prospects Researchers are designing COFs with biodegradable components, refining synthesis techniques to reduce toxic byproducts, and creating effective regeneration techniques that lessen the release of hazardous substances into the environment to ensure environmental compatibility and minimal toxicity. For the safe and long-term usage of COFs in water treatment applications, including PFAS adsorption, several factors must be taken into consideration. For instance, microorganisms can have a variety of effects on the recyclability and performance of COFs in treatment systems, including biofouling, biodegradation, regeneration, and structural stability. Although COFs are normally intended to be chemically stable, certain microbial communities may have the ability to biodegrade or change the structure of COFs over time (Li et al. 2023d). Furthermore, microbes can stick to the surfaces of COFs, resulting in biofouling. This can clog the pores of the COF, limiting its effectiveness and even affecting its structural integrity over time (Ampong et al. 2024). Besides, microorganism-produced biofilms may interfere with COF adsorption and filtering capacities. This may impact their performance and recyclability, necessitating more frequent regeneration or replacement. To overcome these difficulties, efforts should be undertaken to improve COFs' microbial resistance, such as integrating antimicrobial agents or designing COFs with structures that are less vulnerable to microbial activity. Lastly, regular maintenance, microbial growth monitoring, and effective regeneration processes will be critical to ensuring COF effectiveness and recyclability in treatment systems. Moreover, COFs may perform even better in PFAS adsorption if they are integrated with other materials or technologies. Furthermore, interdisciplinary cooperation among chemists, environmental engineers, and material scientists might spur advancements in COF use and design for PFAS cleanup.

### Conclusion

COFs have emerged as desirable candidates for the removal of PFASs from polluted sources. This is due to their special qualities, which include large surface area, adjustable porosity, various chemical functions, and regenerability. To selectively adsorb PFASs from polluted sources. COFs with excellent functionalities can be created by direct synthesis, post-synthetic modification, in situ synthesis, condensation reaction, and Schiff base condensation. Solvothermal synthesis is currently the main direct synthetic method, producing COFs with high efficiency for PFAS adsorption and tunable characteristics. The strong affinity of  $\beta$ -CD, amine-functionalised, porphyrin-based, ionic, and hydrophobic COFs for PFASs enables the efficient adsorption and removal of these persistent pollutants. Not only do COFs exhibit superior extraction efficiency, but they also demonstrate superior PFAS selectivity. The electrostatic interaction between the positively charged sites on COFs and the negatively charged functional groups on PFAS molecules facilitates easy adsorption or binding of PFAS onto the COF surface can happen. Besides, through host-guest chemistry and hydrophobic interactions, COFs form inclusion complexes with PFASs, therefore improving their adsorption. Analysis of current literature suggests that ionic COFs and aminefunctionalised COFs tend to have higher PFAS adsorption capacities due to their functionalisation promoting strong interactions with these substances. Despite ongoing research into COF-based composite materials, their development is still in its early stages, with several challenges to overcome, including environmental compatibility and toxicity, longterm stability and regeneration, and synthesis scalability, to improve their prospects in current and future research.

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

Ethical approval Not applicable.

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### References

- Abaie E, Kumar M, Kumar N, Sun Y, Guelfo J, Shen Y, Reible D (2024) Application of β-cyclodextrin adsorbents in the removal of mixed per-and polyfluoroalkyl substances. Toxics 12(4):264. https://doi.org/10.3390/TOXICS12040264/S1
- Abuzeid HR, EL-Mahdy AF, Kuo SW (2021) Covalent organic frameworks: design principles, synthetic strategies, and diverse applications. Giant 6:100054. https://doi.org/10.1016/j.giant.2021. 100054
- Adams M, Issaka E, Chen C (2024) Anammox-based technologies: a review of recent advances, mechanism, and bottlenecks. J Environ Sci (China) 148:151–173. https://doi.org/10.1016/j.jes.2024. 01.015
- Ajmal Z, Kizito S, Alalwan B et al (2024) Recent advances in COFbased framework: synthesis, potential application, current challenges and future direction. Mater Today Chem 39:102140. https://doi.org/10.1016/j.mtchem.2024.102140
- Al-dolaimy F, Saraswat SK, Hussein BA et al (2024) A review of recent advancement in covalent organic framework (COFs) synthesis and characterization with a focus on their applications in antibacterial activity. Micron 179:103595. https://doi. org/10.1016/j.micron.2024.103595
- AlNeyadi SS, Seeta SA, Aljasmi SN, Alshkeili DS, Al Anoud MH, Salama OS (2024) Ibuprofen removal from water using the IB-COF covalent organic framework. J Hazard Mater Adv 15:100451. https://doi.org/10.1016/j.hazadv.2024.100451
- Alsudairy Z, Brown N, Yang C et al (2023) Facile microwaveassisted synthesis of 2D imine-linked covalent organic frameworks for exceptional iodine capture. Precis Chem 1:233– 240. https://doi.org/10.1021/PRECHEM.3C00006/ASSET/ IMAGES/LARGE/PC3C00006\_0003.JPEG
- Ampong DN, Effah E, Tsiwah EA et al (2024) Advances and challenges in covalent organic frameworks as an emerging class of materials for energy and environmental concerns. Coord Chem Rev 519:216121. https://doi.org/10.1016/J.CCR.2024.216121
- Antipova ML, Odintsova EG, Petrenko VE (2024) Behavior of β-cyclodextrin/naproxen inclusion complex in supercritical carbon dioxide. Computer simulation. J Mol Liq 407:125234. https://doi.org/10.1016/j.molliq.2024.125234
- Asayesh-Ardakani E, Rahmani M, Hosseinian A, Ghaffari SB, Sarrafzadeh MH (2024) Improvement strategies on application of covalent organic frameworks in adsorption, photocatalytic, and membrane processes for organic pollution removal from water. Coord Chem Rev 518:216087. https://doi.org/10.1016/j. ccr.2024.216087
- Ateia M, Alsbaiee A, Karanfil T, Dichtel W (2019a) Efficient PFAS removal by amine-functionalized sorbents: critical review of the current literature. Environ Sci Technol Lett 6:688–695. https://doi.org/10.1021/ACS.ESTLETT.9B00659/SUPPL\_ FILE/EZ9B00659\_SI\_001.PDF

- Ateia M, Alsbaiee A, Karanfil T, Dichtel W (2019b) Efficient PFAS removal by amine-functionalized sorbents: critical review of the current literature. Environ Sci Technol Lett 6:688–695. https://doi.org/10.1021/ACS.ESTLETT.9B00659
- Bagheri AR, Aramesh N (2021) Towards the room-temperature synthesis of covalent organic frameworks: a mini-review. J Mater Sci 56:1116–1132. https://doi.org/10.1007/S10853-020-05308-9/TABLES/2
- Bei Y, Deng S, Du Z et al (2014) Adsorption of perfluorooctane sulfonate on carbon nanotubes: Influence of pH and competitive ions. Water Sci Technol 69:1489–1495. https://doi.org/10. 2166/WST.2014.049
- Ben H, Du W, Zhao J et al (2024a) Ionic covalent organic frameworks: from synthetic strategies to advanced electro-, photo-, and thermo- energy functionalities. Coord Chem Rev 517:216003. https://doi.org/10.1016/j.ccr.2024.216003
- Ben H, Du W, Zhao J et al (2024b) Ionic covalent organic frameworks: from synthetic strategies to advanced electro-, photo-, and thermo- energy functionalities. Coord Chem Rev 517:216003. https://doi.org/10.1016/J.CCR.2024.216003
- Bhambri H, Khullar S, Sakshi MSK (2022) Nitrogen-rich covalent organic frameworks: a promising class of sensory materials. Mater Adv 3:19–124. https://doi.org/10.1039/D1MA00506E
- Björneholm O, Öhrwall G, De Brito AN et al (2022) Superficial tale of two functional groups: on the surface propensity of aqueous carboxylic acids, alkyl amines, and amino acids. Acc Chem Res 55:3285. https://doi.org/10.1021/ACS.ACCOUNTS. 2C00494
- Brown N, Alsudairy Z, Behera R et al (2023) Green mechanochemical synthesis of imine-linked covalent organic frameworks for high iodine capture. Green Chem 25:6287–6296. https://doi.org/10. 1039/D3GC01927F
- Bügel S, Hähnel M, Kunde T, de Sousa AN, Sun Y, Spieß A, Beglau TH, Schmidt BM, Janiak C (2022) Synthesis and characterization of a crystalline imine-based covalent organic framework with triazine node and biphenyl linker and its fluorinated derivate for CO<sub>2</sub>/CH<sub>4</sub> separation. Materials 15(8):2807. https://doi.org/10. 3390/MA15082807/S1
- Calore F, Badetti E, Bonetto A et al (2024) Non-conventional sorption materials for the removal of legacy and emerging PFAS from water: a review. Emerg Contam 10:100303. https://doi.org/10. 1016/j.emcon.2024.100303
- Cao Y, Mou Y, Zhang J et al (2024) Porphyrin-based frameworks and derivatives for the oxygen reduction reaction. Mater Today Catal 4:100044. https://doi.org/10.1016/j.mtcata.2024.100044
- Chen M, Li H, Liu C et al (2021) Porphyrin- and porphyrinoid-based covalent organic frameworks (COFs): from design, synthesis to applications. Coord Chem Rev 435:213778. https://doi.org/10. 1016/j.ccr.2021.213778
- Chen S, Zhu J, Ma C et al (2024) Mercapto-β-cyclodextrin covalent organic frameworks for enantioselective liquid-liquid extraction. Coll Surf A Physicochem Eng Asp 687:133496. https://doi.org/ 10.1016/J.COLSURFA.2024.133496
- Cohn BA, La Merrill MA, Krigbaum NY et al (2020) In utero exposure to poly– and perfluoroalkyl substances (PFASs) and subsequent breast cancer. Reprod Toxicol 92:112–119. https://doi.org/10. 1016/J.REPROTOX.2019.06.012
- Dan A, Zhang S, Chen Z, Dong J, Zheng W, Tu Y, Lin Z, Cai Z (2023) Facile synthesis of Cu<sup>2+</sup>-immobilized magnetic covalent organic frameworks for highly efficient enrichment and sensitive determination of five phthalate monoesters from mouse plasma with HPLC-MS/MS. Talanta 253:123923. https://doi.org/10.1016/j. talanta.2022.123923
- Das R, Verma PK, Nagaraja CM (2024) Design of porphyrin-based frameworks for artificial photosynthesis and environmental

remediation: recent progress and future prospects. Coord Chem Rev 514:215944. https://doi.org/10.1016/j.ccr.2024.215944

- Dautzenberg E, Li G, de Smet LCPM (2023) Aromatic amine-functionalized covalent organic frameworks (COFs) for CO<sub>2</sub>/N<sub>2</sub> separation. ACS Appl Mater Interf 15:5118–5127. https://doi.org/10. 1021/ACSAMI.2C17672
- Deng L, Ding Z, Ye X, Jiang D (2022) Covalent organic frameworks: chemistry of pore interface and wall surface perturbation and impact on functions. Acc Mater Res 3:879–893. https://doi.org/ 10.1021/ACCOUNTSMR.2C00108
- Du Y, Calabro D, Wooler B et al (2015) One step facile synthesis of amine-functionalized cof-1 with enhanced hydrostability. Chem Mater 27:1445–1447. https://doi.org/10.1021/CM5032317
- Emmanuel SS, Olawoyin CO, Adesibikan AA, Nafiu SA (2023) Solvothermally and non-solvthermally fabricated covalent organic frameworks (COFs) for eco-friendly remediation of radiocontaminants in aquatic environments: a review. J Organomet Chem 1005:122984. https://doi.org/10.1016/j.jorganchem.2023.122984
- Fan C, Zhang L, Kong Y et al (2023) Solid-state synthesis of intrinsically proton-conducting covalent organic framework membrane. J Memb Sci 676:121610. https://doi.org/10.1016/J.MEMSCI. 2023.121610
- Gharanli S, Malekshah RE, Moharramnejad M, Ehsani A, Shahi M, Joshaghani AH et al (2024) Recent progress in designing heterogeneous COFs with the photocatalytic performance. Mol Catal 560:114127. https://doi.org/10.1016/j.mcat.2024.114127
- Ghosh A, Nag D, Chatterjee R et al (2024) CO2 to dimethyl ether (DME): structural and functional insights of hybrid catalysts. Catal Sci Technol 14:1387–1427. https://doi.org/10.1039/ D3CY01497E
- Gong J, Zhang X, Liang R et al (2024) Rapidly enrichment and detection of per-and polyfluoroalkyl substances in foods using a novel bifunctional covalent organic framework. Food Chem 447:139016. https://doi.org/10.1016/j.foodchem.2024.139016
- Grunenberg L, Savasci G, Terban MW et al (2021) Amine-linked covalent organic frameworks as a platform for postsynthetic structure interconversion and pore-wall modification. J Am Chem Soc 143:3430–3438. https://doi.org/10.1021/JACS.0C12249/ASSET/ IMAGES/LARGE/JA0C12249\_0004.JPEG
- Haase F, Lotsch BV (2020) Solving the COF trilemma: towards crystalline, stable and functional covalent organic frameworks. Chem Soc Rev 49:8469–8500. https://doi.org/10.1039/D0CS01027H
- Hao L, Shen R, Liang G et al (2024) Precise local functionalization of covalent organic framework for efficient carrier separation in photocatalytic H<sub>2</sub> evolution. Appl Catal b: Environ Energy 348:123837. https://doi.org/10.1016/J.APCATB.2024.123837
- Hayat A, Raza S, Amin MA et al (2024) Developing new-generation covalent organic frameworks as sustainable catalysts: synthesis, properties, types and solar energy production. Mater Sci Eng R: Rep 157:100771. https://doi.org/10.1016/j.mser.2024.100771
- He N, Li Z, Hu C, Chen Z (2022a) In situ synthesis of a spherical covalent organic framework as a stationary phase for capillary electrochromatography. J Pharm Anal 12:610–616. https://doi.org/10.1016/J.JPHA.2022.06.005
- He C, Yang Y, Hou YJ et al (2022b) Chitosan-coated fluoro-functionalized covalent organic framework as adsorbent for efficient removal of per- and polyfluoroalkyl substances from water. Sep Purif Technol 294:121195. https://doi.org/10.1016/J.SEPPUR. 2022.121195
- Herath A, Salehi M, Jansone-Popova S (2022) Production of polyacrylonitrile/ionic covalent organic framework hybrid nanofibers for effective removal of chromium(VI) from water. J Hazard Mater 427:128167. https://doi.org/10.1016/j.jhazmat.2021.128167
- Hou YJ, Deng J, He K et al (2020a) Covalent organic frameworksbased solid-phase microextraction probe for rapid and ultrasensitive analysis of trace per- and polyfluoroalkyl substances using

mass spectrometry. Anal Chem 92:10213–10217. https://doi. org/10.1021/ACS.ANALCHEM.0C01829/ASSET/IMAGES/ LARGE/AC0C01829\_0005.JPEG

- Hou Y-J, Deng J, He K et al (2020b) Covalent organic frameworksbased solid-phase microextraction probe for rapid and ultrasensitive analysis of trace per- and polyfluoroalkyl substances using mass spectrometry. Anal Chem 92:10213–10217. https://doi.org/ 10.1021/acs.analchem.0c01829
- Issaka E (2024) From complex molecules to harmless byproducts: electrocoagulation process for water contaminants degradation. Desal Water Treat 319:100532. https://doi.org/10.1016/j.dwt. 2024.100532
- Issaka E, Amu-Darko JNO (2024) Biomimetic nanoparticles for cancer therapy: a review of recent advances, applications, and bottlenecks. Biomed Mater Dev. https://doi.org/10.1007/ s44174-024-00179-z
- Issaka E, Fapohunda FO, Amu-Darko JNO et al (2022) Biochar-based composites for remediation of polluted wastewater and soil environments: challenges and prospects. Chemosphere 297:134163. https://doi.org/10.1016/j.chemosphere.2022.134163
- Issaka E, Amu-Darko JN, Yakubu S, Fapohunda FO, Ali N, Bilal M (2022) Advanced catalytic ozonation for degradation of pharmaceutical pollutants-A review. Chemosphere 289:133208. https:// doi.org/10.1016/j.chemosphere.2021.133208
- Issaka E, Amu-Darko JNO, Adams M et al (2023) Zinc imidazolate metal-organic frameworks-8-encapsulated enzymes/nanoenzymes for biocatalytic and biomedical applications. Catal Lett 153:2083–2106. https://doi.org/10.1007/s10562-022-04140-x
- Issaka E, Danso-Boateng E, Baffoe J (2024) Harnessing the power of heterogeneous photocatalytic process for sustainable pharmaceutical contaminant remediation in water environments. Desal Water Treat 319:100574. https://doi.org/10.1016/J.DWT.2024. 100574
- Ji W, Xiao L, Ling Y et al (2018) Removal of GenX and perfluorinated alkyl substances from water by amine-functionalized covalent organic frameworks. J Am Chem Soc 140:12677–12681. https:// doi.org/10.1021/JACS.8B06958
- Ji W, Guo YS, Xie HM et al (2020) Rapid microwave synthesis of dioxin-linked covalent organic framework for efficient microextraction of perfluorinated alkyl substances from water. J Hazard Mater 397:122793. https://doi.org/10.1016/J.JHAZMAT. 2020.122793
- Jiang L, Bao F, Peng Y et al (2024) Porphyrin-based Schiff-base and aminal nitrogen-rich porous organic polymers for capture of SO<sub>2</sub> and CO<sub>2</sub>. Microporous Mesoporous Mater 381:113338. https:// doi.org/10.1016/J.MICROMESO.2024.113338
- Karbassiyazdi E, Kasula M, Modak S, Pala J, Kalantari M, Altaee A, Esfahani MR, Razmjou A (2023) A juxtaposed review on adsorptive removal of PFAS by metal-organic frameworks (MOFs) with carbon-based materials, ion exchange resins, and polymer adsorbents. Chemosphere 311:136933. https://doi.org/ 10.1016/j.chemosphere.2022.136933
- Kong X, Wu Z, Strømme M, Xu C (2024) Ambient aqueous synthesis of imine-linked covalent organic frameworks (COFs) and fabrication of freestanding cellulose nanofiber@COF nanopapers. J Am Chem Soc 146:742–751. https://doi.org/10.1021/JACS. 3C10691/ASSET/IMAGES/LARGE/JA3C10691\_0004.JPEG
- Lan Z, Huang J, Fu S, Chen Y, Meng T, Zhou W, Xu Z, Chen M, Wen L, Cheng Y, Ding L (2024a) Length-controlled hydrophobic CF<sub>3</sub>-COF as a highly efficient absorbent coating for dual-mode solid-phase microextraction of sixteen polycyclic aromatic hydrocarbons in water samples. Sci Total Environ 925:171726. https://doi.org/10.1016/j.scitotenv.2024.171726
- Lan Z, Huang J, Fu S et al (2024b) Length-controlled hydrophobic CF<sub>3</sub>-COF as a highly efficient absorbent coating for dual-mode solid-phase microextraction of sixteen polycyclic aromatic

hydrocarbons in water samples. Sci Total Environ 925:171726. https://doi.org/10.1016/J.SCITOTENV.2024.171726

- Li PZ, Wang XJ, Zhao Y (2019) Click chemistry as a versatile reaction for construction and modification of metal-organic frameworks. Coord Chem Rev 380:484–518. https://doi.org/ 10.1016/j.ccr.2018.11.006
- Li Y, Wang C, Ma S et al (2021) Facile fabrication of hollow tubular covalent organic frameworks using decomposable monomer as building block. RSC Adv 11:20899–20910. https://doi.org/10. 1039/D1RA02104D
- Li W, Shen M, Yu YJ et al (2022) Superhydrophobic covalent organic frameworks prepared via nucleophilic substitution reaction for effective oil/water separation. Coll Surf A Physicochem Eng Asp 655:130239. https://doi.org/10.1016/j.colsu rfa.2022.130239
- Li HZ, Yang C, Qian HL, Yan XP (2023a) Room-temperature synthesis of ionic covalent organic frameworks for efficient removal of diclofenac sodium from aqueous solution. Sep Purif Technol 306:122704. https://doi.org/10.1016/J.SEPPUR.2022.122704
- Li K, Quan X, Yan B (2023b) Eu(III)-functionalized iCOF hybrids by "tandem post-synthetic modifications" for fluorescent detection of folic acid and trimethoprim: a logical judgment by combination of neural networks and logic gates. Sens Actuators B Chem 392:134078. https://doi.org/10.1016/j.snb.2023.134078
- Li H, Junker AL, Wen J et al (2023c) A recent overview of per- and polyfluoroalkyl substances (PFAS) removal by functional framework materials. Chem Eng J 452:139202. https://doi.org/10. 1016/j.cej.2022.139202
- Li T, Wang D, Guo Z et al (2023d) Biodegradable covalent organic frameworks achieving tumor micro-environment responsive drug release and antitumor treatment. Biomater Sci 11:6524–6536. https://doi.org/10.1039/D3BM01088K
- Li R, Sun F, Liu Z et al (2024a) Research progress and prospect of covalent organic frameworks (COFs) and composites: from synthesis to application in water contaminants. J Environ Chem Eng 12:113944. https://doi.org/10.1016/j.jece.2024.113944
- Li W, Wang Y, Li L et al (2024b) Promoting energy transfer pathway in porphyrin-based sp<sup>2</sup> carbon-conjugated covalent organic frameworks for selective photocatalytic oxidation of sulfide. Chin J Struct Chem 43:100299. https://doi.org/10.1016/j.cjsc. 2024.100299
- Li H, Liu J, Wang Y, Guo C, Pi Y, Fang Q, Liu J (2025) Hollow covalent organic framework (COF) nanoreactors for sustainable photo/electrochemical catalysis. Coord Chem Rev 523:216240. https://doi.org/10.1016/j.ccr.2024.216240
- Liu J, Li G, Wang P (2022) Thiol-ene click synthesis of β-cyclodextrinfunctionalized covalent organic framework-based magnetic nanocomposites (Fe3O4@COF@β-CD) for solid-phase extraction and determination of estrogens and estrogen mimics. Microchem J 174:106987. https://doi.org/10.1016/J.MICROC.2021.106987
- Liu Q, Zou Y, Yang Y et al (2023a) Fabrication of a novel dual-emission fluorescence covalent organic framework and its luminescent hybrid hydrogel material: application in the detection and adsorption of eriochrome azo anionic dyes. Mater Today Chem 34:101810. https://doi.org/10.1016/j.mtchem.2023.101810
- Liu S, Hu Z, Yan X et al (2023b) Separation and purification of target flavonoids using covalently connected MOFs@boronic acidfunctionalized-COFs magnetic hybrids: precise identification and enhanced stability. Sep Purif Technol 320:124061. https:// doi.org/10.1016/J.SEPPUR.2023.124061
- Lohse MS, Bein T, Lohse MS, Bein T (2018) Covalent organic frameworks: structures, synthesis, and applications. Adv Funct Mater 28:1705553. https://doi.org/10.1002/ADFM.201705553
- Maleki B, Esmaeili H, Venkatesh YK, Yusuf M (2024) A critical review on MOFs and COFs-based heterogeneous catalysts in biodiesel generation: synthesis methods, structural features,

mechanisms, kinetic, economic/environmental evaluation, and their performance. Process Saf Environ Prot 187:903–925. https://doi.org/10.1016/j.psep.2024.04.144

- Manzoor MH, Naz N, Naqvi SMG et al (2024) Wastewater treatment using metal-organic frameworks (MOFs). Appl Mater Today 40:102358. https://doi.org/10.1016/J.APMT.2024.102358
- Martín-Illán J, Rodríguez-San-Miguel D, Rodríguez-San-Miguel D et al (2020) Green synthesis of imine-based covalent organic frameworks in water. Chem Commun 56:6704–6707. https://doi. org/10.1039/D0CC02033H
- Martín-Illán J, Rodríguez-San-Miguel D, Zamora F (2023) Evolution of covalent organic frameworks: from design to real-world applications. Coord Chem Rev 495:215342. https://doi.org/10.1016/J. CCR.2023.215342
- Mo F, Zhou Q, Wang Q et al (2022) The applications of MOFs related materials in photo/electrochemical decontamination: an updated review. Chem Eng J 450:138326. https://doi.org/10.1016/j.cej. 2022.138326
- Mushtaq N, Ahmad A, Wang X, Khan U, Gao J (2024) MOFs/COFs hybrids as next-generation materials for electrocatalytic CO<sub>2</sub> reduction reaction. Chem Eng J 486:150098. https://doi.org/10. 1016/j.cej.2024.150098
- Nazir MA, Naseer M, Ullah S, Ahmad K, Ismail MA, Iqbal R, Najam T, Rosaiah P, Raza MA, Shah SS (2024) Designing MOF–COF hybrid materials for energy, biomedical and environment applications. Inorg Chem Commun 170:113262. https://doi.org/10. 1016/j.inoche.2024.113262
- Olsen GW (2015) PFAS biomonitoring in higher exposed populations. Mol Integr Toxicol. https://doi.org/10.1007/ 978-3-319-15518-0\_4
- Osman AI, Ayati A, Farrokhi M, Khadempir S, Rajabzadeh AR, Farghali M, Krivoshapkin P, Tanhaei B, Rooney DW, Yap PS (2024) Innovations in hydrogen storage materials: synthesis, applications, and prospects. J Energy Storage 95:112376. https://doi. org/10.1016/j.est.2024.112376
- Oudi S, Oveisi AR, Daliran S et al (2023) A porphyrin-based covalent organic framework as metal-free visible-LED-Light photocatalyst for one-pot tandem benzyl alcohol oxidation/knoevenagel condensation. Nanomaterials 13:558. https://doi.org/10.3390/ NANO13030558/S1
- Park M, Wu S, Lopez IJ et al (2020) Adsorption of perfluoroalkyl substances (PFAS) in groundwater by granular activated carbons: roles of hydrophobicity of PFAS and carbon characteristics. Water Res 170:115364. https://doi.org/10.1016/J.WATRES. 2019.115364
- Peng W, Qing D, Wu J, Zhou P, Wu D, Tian S, He Y (2025) Ultrahydrophilic MOF-303 on electrospun nanofibers with Burr puzzles structure for the purification of oily wastewater containing heavy metal ions. J Membr Sci 713:123289. https://doi. org/10.1016/j.memsci.2024.123289
- Qian HL, Yang J, Yang C et al (2024) Photothermal porphyrin-based covalent organic framework for efficient removal of perfluoroalkyl substances. Sep Purif Technol 331:125567. https://doi. org/10.1016/J.SEPPUR.2023.125567
- Rejali NA, Dinari M, Wang Y (2023) Post-synthetic modifications of covalent organic frameworks (COFs) for diverse applications. Chem Commun 59:11631–11647. https://doi.org/10. 1039/D3CC03091A
- Ren LY, Geng TM (2024) Constructing cationic flexible covalent organic frameworks through post-functionalization for enhancing the iodine adsorption capacity. Chem Eng J 480:148076. https://doi.org/10.1016/j.cej.2023.148076
- Ross I, McDonough J, Miles J et al (2018) A review of emerging technologies for remediation of PFASs. Remediat J 28:101– 126. https://doi.org/10.1002/rem.21553

- Sahu KM, Patra S, Swain SK (2023) Host-guest drug delivery by β-cyclodextrin assisted polysaccharide vehicles: a review. Int J Biol Macromol 240:124338. https://doi.org/10.1016/j.ijbio mac.2023.124338
- Segura JL, Mancheño MJ, Zamora F (2016) Covalent organic frameworks based on Schiff-base chemistry: synthesis, properties and potential applications. Chem Soc Rev 45:5635–5671. https://doi.org/10.1039/C5CS00878F
- Segura JL, Royuela S, Mar Ramos M (2019) Post-synthetic modification of covalent organic frameworks. Chem Soc Rev 48:3903– 3945. https://doi.org/10.1039/C8CS00978C
- Shah IA, Bilal M, Ihsanullah I et al (2023) Revolutionizing water purification: Unleashing graphene oxide (GO) membranes. J Environ Chem Eng. https://doi.org/10.1016/j.jece.2023.111450
- Shan Z, Sun Y, Wu M et al (2024) Metal-porphyrin-based threedimensional covalent organic frameworks for electrocatalytic nitrogen reduction. Appl Catal B 342:123418. https://doi.org/ 10.1016/j.apcatb.2023.123418
- Sharma N, Kumar V, Sugumar V et al (2024) A comprehensive review on the need for integrated strategies and process modifications for per- and polyfluoroalkyl substances (PFAS) removal: current insights and future prospects. Case Stud Chem Environ Eng 9:100623. https://doi.org/10.1016/j.cscee. 2024.100623
- Singh K, Kumar N, Yadav AK, Singh R, Kumar K (2023) Per-and polyfluoroalkyl substances (PFAS) as a health hazard: current state of knowledge and strategies in environmental settings across Asia and future perspectives. Chem Eng J 475:145064. https://doi.org/ 10.1016/j.cej.2023.145064
- Singh A, Soorya KK, Bhatnagar A, Gupta AK (2024) Crystalline porous frameworks: advances in synthesis, mechanisms, modifications, and remediation of organic pollutants. Sep Purif Technol 353:128588. https://doi.org/10.1016/j.seppur.2024.128588
- Singh AR, Mohan B, Raghav N et al (2024) Understanding the mechanisms and applications of luminescent covalent organic frameworks (COFs) for multi-analyte sensing. J Mol Struct 1321:139945. https://doi.org/10.1016/J.MOLSTRUC.2024. 139945
- Song JH, Kang DW (2023) Hazardous nitroaromatic explosives detection by emerging porous solid sensors. Coord Chem Rev 492:215279. https://doi.org/10.1016/j.ccr.2023.215279
- Song X, Wang R, Wang X et al (2022) An amine-functionalized olefin-linked covalent organic framework used for the solid-phase microextraction of legacy and emerging per- and polyfluoroalkyl substances in fish. J Hazard Mater 423:127226. https://doi.org/ 10.1016/J.JHAZMAT.2021.127226
- Sun X, Ji W, Hou S, Wang X (2020) Facile synthesis of trifluoromethyl covalent organic framework for the efficient microextraction of per-and polyfluorinated alkyl substances from milk products. J Chromatogr A 1623:461197. https://doi.org/10. 1016/J.CHROMA.2020.461197
- Sun X, Wang R, Li L et al (2021) Online extraction based on ionic covalent organic framework for sensitive determination of trace per- and polyfluorinated alkyl substances in seafoods by UHPLC-MS/MS. Food Chem 362:130214. https://doi.org/10. 1016/j.foodchem.2021.130214
- Sun M, Feng J, Feng Y et al (2022) Preparation of ionic covalent organic frameworks and their applications in solid-phase extraction. TrAC–Trends Anal Chem 157:116829. https://doi. org/10.1016/j.trac.2022.116829
- Szymańska A, Dutkiewicz M, Maciejewski H (2024) Thiol-isocyanate click reaction for rapid and efficient generation of a library of organofunctional silanes. Organometallics 43:1349– 1354. https://doi.org/10.1021/ACS.ORGANOMET.4C00086/ ASSET/IMAGES/LARGE/OM4C00086\_0008.JPEG

- Tang S, Qin X, Lv Y et al (2022) Adsorption of three perfluoroalkyl sulfonate compounds from environmental water and human serum samples using cationic porous covalent organic framework as adsorbents and detection combination with MALDI-TOF MS. Appl Surf Sci 601:154224. https://doi.org/10.1016/j. apsusc.2022.154224
- Tang X, Yang Y, Li X et al (2023) Postmodification of an aminefunctionalized covalent organic framework for enantioselective adsorption of tyrosine. ACS Appl Mater Interf 15:24836– 24845. https://doi.org/10.1021/ACSAMI.3C02025
- Thompson D, Zolfigol N, Xia Z, Lei Y (2024) Recent progress in per- and polyfluoroalkyl substances (PFAS) sensing: a critical mini-review. Sens Actuators Rep 7:100189. https://doi.org/10. 1016/j.snr.2024.100189
- Umeh AC, Hassan M, Egbuatu M et al (2023) Multicomponent PFAS sorption and desorption in common commercial adsorbents: Kinetics, isotherm, adsorbent dose, pH, and index ion and ionic strength effects. Sci Total Environ 904:166568. https://doi.org/ 10.1016/j.scitotenv.2023.166568
- Vakili M, Cagnetta G, Deng S et al (2024) Regeneration of exhausted adsorbents after PFAS adsorption: A critical review. J Hazard Mater 471:134429. https://doi.org/10.1016/J.JHAZMAT.2024. 134429
- Vardhan H, Rummer G, Deng A, Ma S (2023) Large-scale synthesis of covalent organic frameworks: challenges and opportunities. Membranes 13(8):696. https://doi.org/10.3390/MEMBR ANES13080696
- Walkowiak-Kulikowska J (2022) Poly/Perfluorinated alkyl substances (PFASs)–Synthetic methods, properties and applications
- Wang Y, Wu S, Wu D et al (2020) Amino bearing core-shell structured magnetic covalent organic framework nanospheres: preparation, postsynthetic modification with phenylboronic acid and enrichment of monoamine neurotransmitters in human urine. Anal Chim Acta 1093:61–74. https://doi.org/10.1016/J. ACA.2019.09.078
- Wang W, Shao H, Zhou S et al (2021a) Rapid removal of perfluoroalkanesulfonates from water by β-cyclodextrin covalent organic frameworks. ACS Appl Mater Interf 13:48700–48708. https:// doi.org/10.1021/ACSAMI.1C14043/SUPPL\_FILE/AM1C1 4043\_SI\_001.PDF
- Wang W, Zhou Z, Shao H et al (2021b) Cationic covalent organic framework for efficient removal of PFOA substitutes from aqueous solution. Chem Eng J 412:127509. https://doi.org/10. 1016/j.cej.2020.127509
- Wang K, Zhang H, Xiao Y et al (2023a) Efficient exfoliation of covalent organic frameworks by a facile thiol-ene reaction. Chem Eng J 454:140283. https://doi.org/10.1016/j.cej.2022.140283
- Wang W, Zhou S, Jiang X et al (2023b) Fluorinated quaternary ammonium covalent organic frameworks for selective and efficient removal of typical per- and polyfluoroalkyl substances. Chem Eng J 474:145629. https://doi.org/10.1016/j.cej.2023. 145629
- Wang F, Wei C, Miao S et al (2024a) Covalent organic frameworks: multifunctional material in analytical chemistry. Chem Eng J 497:154915. https://doi.org/10.1016/j.cej.2024.154915
- Wang Z, Xie S, Zhang W et al (2024b) Mechanochemical synthesis ionic covalent organic frameworks/cotton composites for pipette tip solid-phase extraction of domoic acid in seafood. Talanta 269:125485. https://doi.org/10.1016/J.TALANTA.2023.125485
- Wang S, Vakili M, Guan T et al (2024c) Adsorption of typical dyes in water by sponge based covalent organic frameworks: pore size and mechanism. Coll Surf A Physicochem Eng Asp 685:133312. https://doi.org/10.1016/J.COLSURFA.2024.133312
- Wei H, Chai S, Hu N et al (2015) The microwave-assisted solvothermal synthesis of a crystalline two-dimensional covalent organic

framework with high CO<sub>2</sub> capacity. Chem Commun 51:12178–12181. https://doi.org/10.1039/C5CC04680G

- Wei J, Shao X, Guo J et al (2024) Rapid and selective removal of aristolochic acid i in natural products by vinylene-linked iCOF resins. J Hazard Mater 461:132140. https://doi.org/10.1016/j. jhazmat.2023.132140
- Wu S, Li Y, Wang T et al (2023) Design and synthesis of dual functional porphyrin-based COFs as highly selective adsorbent and photocatalyst. Chem Eng J 470:144135. https://doi.org/10. 1016/J.CEJ.2023.144135
- Xiao J, Chen J, Liu J et al (2023) Synthesis strategies of covalent organic frameworks: an overview from nonconventional heating methods and reaction media. Green Energy Environ 8:1596– 1618. https://doi.org/10.1016/J.GEE.2022.05.003
- Xie Z, Hu Y, Lin J et al (2023) Calix[4]arene-based covalent organic frameworks with host-guest recognition for selective adsorption of six per- and polyfluoroalkyl substances in food followed by UHPLC-MS/MS detection. J Hazard Mater 459:132198. https:// doi.org/10.1016/J.JHAZMAT.2023.132198
- Xing DY, Chen Y, Zhu J, Liu T (2020) Fabrication of hydrolytically stable magnetic core-shell aminosilane nanocomposite for the adsorption of PFOS and PFOA. Chemosphere 251:126384. https://doi.org/10.1016/J.CHEMOSPHERE.2020.126384
- Xue S, Ma X, Wang Y, Duan G, Zhang C, Liu K, Jiang S (2024) Advanced development of three-dimensional covalent organic frameworks: valency design, functionalization, and applications. Coord Chem Rev 504:215659. https://doi.org/10.1016/j.ccr.2024. 215659
- Yu Z, Chen H, Zhang W et al (2023) Room temperature synthesis of flower-like hollow covalent organic framework for efficient enrichment of microcystins. RSC Adv 13:4255–4262. https:// doi.org/10.1039/D2RA06901F
- Yu L, Dai JY, Xu ZL et al (2024) High-performance COFs composite nanofiltration membrane fabricated by organobase catalyst. Desalination 592:118073. https://doi.org/10.1016/j.desal.2024. 118073
- Zadehnazari A, Khosropour A, Zarei A et al (2024) Viologen-derived covalent organic frameworks: advancing PFAS removal technology with high adsorption capacity. Small. https://doi.org/10. 1002/SMLL.202405176
- Zahmatkesh S, Chen Z, Khan NA, Ni BJ (2024) Removing polyfluoroalkyl substances (PFAS) from wastewater with mixed matrix membranes. Sci Total Environ 912:168881. https://doi.org/10. 1016/j.scitotenv.2023.168881
- Zambzickaite G, Talaikis M, Dobilas J et al (2022) Microwave-assisted solvothermal synthesis of nanocrystallite-derived magnetite spheres. Materials 15:4008. https://doi.org/10.3390/MA151 14008
- Zarei A, Khosropour A, Khazdooz L et al (2024) Substitution and orientation effects on the crystallinity and PFAS adsorption of olefin-linked 2D COFs. ACS Appl Mater Interf 16:9483–9494. https://doi.org/10.1021/ACSAMI.3C17188/SUPPL\_FILE/ AM3C17188\_SI\_002.MOV
- Zeppuhar AN, Rollins DS, Huber DL et al (2023) Linkage transformations in a three-dimensional covalent organic framework for high-capacity adsorption of perfluoroalkyl substances. ACS Appl Mater Interf. https://doi.org/10.1021/acsami.3c12826
- Zhang B, Luo Y, Kanyuck K et al (2018) Facile and template-free solvothermal synthesis of mesoporous/macroporous metal–organic framework nanosheets. RSC Adv 8:33059–33064. https://doi. org/10.1039/C8RA06576D
- Zhang P, Wang Z, Cheng P et al (2021) Design and application of ionic covalent organic frameworks. Coord Chem Rev 438:213873. https://doi.org/10.1016/j.ccr.2021.213873
- Zhang Q, Zhu N, Lu Z et al (2024a) Magnetic covalent organic frameworks as sorbents in the chromatographic analysis of

environmental organic pollutants. J Chromatogr A 1728:465034. https://doi.org/10.1016/j.chroma.2024.465034

- Zhang X, Wang S, Zhu X et al (2024b) Efficient removal of per/polyfluoroalkyl substances from water using recyclable chitosancoated covalent organic frameworks: experimental and theoretical methods. Chemosphere 356:141942. https://doi.org/10. 1016/J.CHEMOSPHERE.2024.141942
- Zhang S, Ding J, Tian D et al (2024c) Adsorption behavior and mechanism of NH<sub>2</sub>-MIL-101(Cr)@COFs@SA composite adsorbent for tetracycline removal. Polymer (Guildf) 312:127631. https://doi. org/10.1016/J.POLYMER.2024.127631
- Zhang X, Wang S, Zhu X, Zhu D, Wang W, Wang B, Deng S, Yu G (2024d) Efficient removal of per/polyfluoroalkyl substances from water using recyclable chitosan-coated covalent organic frameworks: experimental and theoretical methods. Chemosphere 356:141942. https://doi.org/10.1016/J.CHEMOSPHERE.2024.141942
- Zhang L, Han H, Zhou J et al (2024e) Imprinted covalent organic frameworks solid-phase microextraction fiber for in vivo monitoring of acidic per- and polyfluoroalkyl substances in live aloe. Sci Total Environ 918:170645. https://doi.org/10.1016/j.scito tenv.2024.170645
- Zhang X, Liu J, Zhang H et al (2025) Highly selective guanidine-linked covalent organic framework for efficient removal of perfluoroalkyl carboxylic acids from water samples. Sep Purif Technol 357:130039. https://doi.org/10.1016/J.SEPPUR.2024.130039
- Zhao W, Yan P, Yang H et al (2022) (2022) Using sound to synthesize covalent organic frameworks in water. Nat Synth 1(1):87–95. https://doi.org/10.1038/s44160-021-00005-0

- Zhao K, Zhao X, Lu Q et al (2024) Porphyrin-based COF nanosheet arrays with donor-acceptor structure for solar-driven water purification. Desalination 588:117956. https://doi.org/10.1016/j.desal. 2024.117956
- Zhu D, Zhu Y, Yan Q et al (2021) Pure crystalline covalent organic framework aerogels. Chem Mater 33:4216–4224. https://doi.org/ 10.1021/ACS.CHEMMATER.1C01122/SUPPL\_FILE/CM1C0 1122\_SI\_002.MP4
- Zhu L, Zhu H, Wang L et al (2023) Efficient proton conduction in porous and crystalline covalent-organic frameworks (COFs). J Energy Chem 82:198–218. https://doi.org/10.1016/j.jechem. 2023.04.002
- Zhu Y, Chen L, Pan J et al (2024) Recent advances in COF-derived carbon materials: Synthesis, properties, and applications. Prog Mater Sci. https://doi.org/10.1016/J.PMATSCI.2024.101373
- Zou J, Fan K, Chen Y et al (2022) Perspectives of ionic covalent organic frameworks for rechargeable batteries. Coord Chem Rev 458:214431. https://doi.org/10.1016/j.ccr.2022.214431

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