



Recent advances in green synthesis of porous organic frameworks

Hao-Ming Wen^{1, #}, Shan Zhang^{1, #}, Ping Li¹, Xinying Kong¹, Rongrong Yuan², Hongming He^{1, *}

Keywords:

Green synthesis, porous organic frameworks, crystalline materials, amorphous materials

Citation: Wen, H. M.; Zhang, S.; Li, P.; Kong, X.; Yuan, R.; He, H. Recent advances in green synthesis of porous organic frameworks. *Chem. Synth.* 2026, 6, 4. <https://dx.doi.org/10.20517/cs.2024.55>

Received: 23 Apr 2024

First Decision: 18 Jun 2024

Revised: 28 Jul 2024

Accepted: 14 Aug 2024

Published: 15 Jan 2026

Academic Editor:

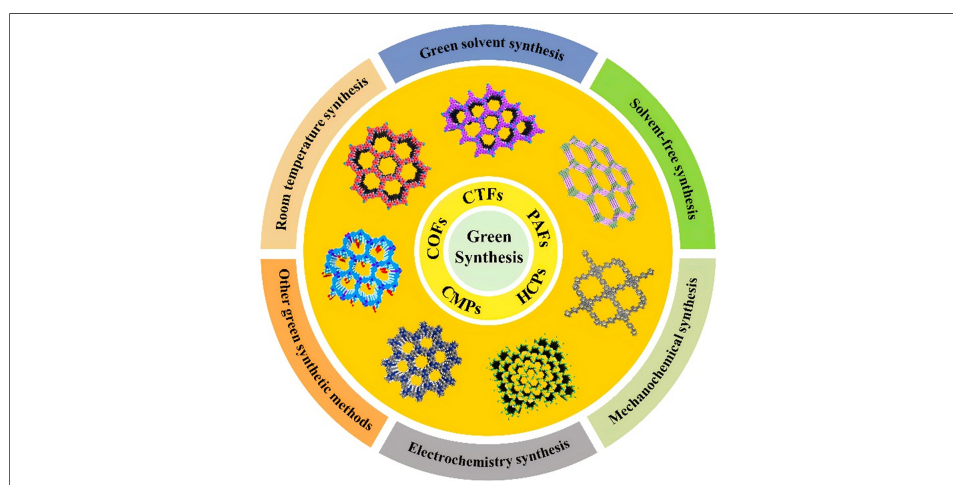
Guangshan Zhu

Copy Editor:

Pei-Yun Wang

Production Editor:

Pei-Yun Wang



Abstract

Recently, porous organic frameworks (POFs) have emerged as functional materials and have been widely used in various applications. Crystalline POFs include covalent organic frameworks (COFs) and partial crystalline covalent triazine frameworks (CTFs). Amorphous porous organic materials are mainly divided into porous aromatic frameworks (PAFs), conjugated microporous polymers (CMPs), and hypercrosslinked porous polymers (HCPs). Although POFs have many unique structural features and excellent performance, the harsh synthesis conditions and difficulty in large-scale production have always limited their widespread use. Therefore, more researchers are paying attention to developing green, energy-saving, and environmentally friendly synthesis processes for large-scale preparation of POFs. Herein, we provide a timely overview on green synthesis of POFs and critically discuss some typical research work in detail. Meanwhile, the green synthesis strategies of POFs are emphatically described to categorize relevant reports. Finally, the challenges and opportunities of green synthetic POFs in the future are proposed according to the above classification research.



¹Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Academy of Interdisciplinary Studies on Intelligent Molecules, College of Chemistry, Tianjin Normal University, Tianjin 300387, China.

²Department of Materials Science and Engineering, Jilin Jianzhu University, Changchun 130118, Jilin, China.

#Authors contributed equally.

*Correspondence to: Dr. Hongming He, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Academy of Interdisciplinary Studies on Intelligent Molecules, College of Chemistry, Tianjin Normal University, Tianjin 300387, China. E-mail: hehongminghz@163.com

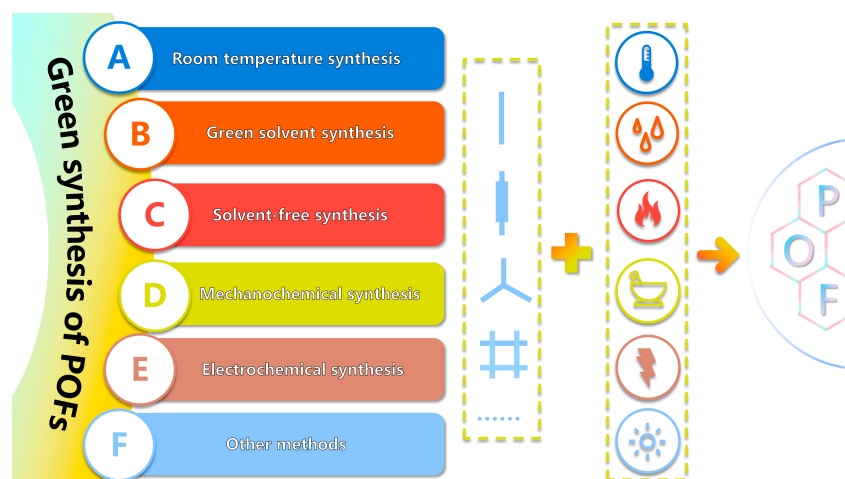
INTRODUCTION

Porous materials, as an important class of functional materials, are formed by two parts: the interconnected solid-state skeleton and the permanent pore generated by gas or liquid phases^[1]. According to the International Union of Pure and Applied Chemistry (IUPAC), they are categorized into three types based on pore size: microporous materials (< 2 nm), mesoporous materials (2–50 nm), and macroporous materials (> 50 nm). Except for the commonly classic inorganic porous materials, such as zeolites^[2,3], porous carbons^[4], mesoporous silicon materials^[5], porous metal materials^[6], and metal-organic frameworks^[7,8], porous organic frameworks (POFs) as a rising class of functional porous materials attract a huge amount of interest from many researchers because of their rich porous structures from micro to mesopores, high specific surface areas, atomic level controllability, and excellent stability^[9]. Generally, POFs are mainly divided into two categories, crystalline and amorphous materials on the basis of their orderliness. The important crystalline materials are covalent organic frameworks (COFs) and partial crystalline covalent triazine frameworks (CTFs) with highly ordered structures^[10,11]. Other classic amorphous POFs principally include three types: porous aromatic frameworks (PAFs)^[12–14], conjugated microporous polymers (CMPs)^[15,16], and hypercrosslinked porous polymers (HCPs)^[17,18]. These porous materials have a certain degree of short-range ordering, but lack long-range ordered structures. Notably, there is no clear boundary for the classification of these amorphous POFs.

The pore structure plays the most important role in different applications of POFs. To construct permanent pore structures and avoid the nonporous phenomenon caused by the dense stacking of organic molecules, the rigid and non-planar organic molecular blocks are always designed and used to form POFs^[19,20]. The pore environment of POFs can be precisely regulated by the molecular size, configuration, functional site, organic coupling method, and synthetic condition^[21,22]. The synthetic reactions are selected according to diverse organic coupling functional groups. The commonly used approaches contain Suzuki coupling^[23], Yamamoto coupling^[24], Schiff-base condensation^[25], Friedel-Crafts alkylation^[26], Sonogashira-Hagihara cross-coupling^[27], Knoevenagel condensation reactions^[28], Ullmann coupling^[29], and aldol condensations^[30].

Although various types of POFs have been extensively prepared to form a large research system, the synthesis of porous materials still faces severe problems. The solvothermal method is the most classical synthesis approach for POFs, but this method has various disadvantages. (1) Harmful organic solvents, such as tritylene, 1,4-dioxane, *N,N*-dimethylformamide, dimethyl sulfoxide and dichlorobenzene, are usually used as reaction media in the reaction system; (2) The operation process is very complex and strict, including cyclic freezing, degassing protection, flame sealing, high temperature, and long reaction time; (3) The synthesis scale is relatively small, making it difficult to meet the needs of large-scale production. In general, the traditional synthesis method includes harsh reaction conditions, high energy consumption, heavy pollution, and small-scale preparation to greatly limit their widespread applications. Hence, it is necessary to develop green and environmentally friendly synthetic strategies for the large-scale preparation of functional POFs.

The concept of green chemistry is proposed in the fields of organic synthesis and industrial chemical processes. In recent years, different green synthesis processes have emerged indirectly in the preparation of POF materials. As an emerging field of importance, only a few reviews focus on green synthesis of COFs^[31,32]. However, there is a lack of novel and systematic summary on the design and preparation of POFs via green synthesis technology. In this review, we summarize the recent advances in green synthesis of POFs and discuss some typical examples in detail [Scheme 1]. Furthermore, the challenges and opportunities of this field in the future are proposed.



Scheme 1. Schematic illustration of the green synthetic strategies for different porous organic materials.

POROUS ORGANIC MATERIALS

Porous organic materials are intrinsic porous materials formed by covalent bonding specific structural units with geometric shapes using a molecular design method^[33]. POFs have the basic characteristics of light weight, abundant pore, good stability, high specific surface area, functional modifiability, *etc.*, so they can be considered as a new class of functional porous materials with outstanding performance in various fields, such as gas separation^[34,35], luminescence sensor^[36,37], heterogeneous catalysis^[38,39], and optoelectronics^[40,41]. To rationally construct POFs with unique structures and excellent functions, it is very important to investigate topological structures and reasonably select appropriate organic monomers, polymerization reactions, and synthesis conditions. Different active sites can be introduced into the organic units to affect POFs and enhance their performance in multiple applications^[42,43]. POFs can be mainly divided into crystalline materials (COFs and CTFs) and amorphous frameworks (PAFs, CMPs, and HCPs) based on the skeleton order degree.

Crystalline porous organic materials

Crystalline porous organic materials with long-range ordered structures and well-defined pores, such as COFs and crystalline CTFs, are widely used as functional materials. These materials attract lots of research interest in various application fields. In fact, crystalline CTFs with special covalent triazine functional groups also belong to COFs^[44,45]. With a deeper understanding of the structures of porous crystalline materials, the suitable covalent bonds between rigid organic monomers play the most important role in forming the crystal skeletons of porous organic materials. Up to now, a growing number of COFs have been widely designed and prepared since the first reported COF in 2005^[46]. Appropriate dynamic covalent bonds are key to preparing crystalline materials. The current main COF materials include four categories: B–O, N–C, C=C, and N=C covalent bonds [Figure 1]. (1) The B–O containing COFs are generated through the self-condensation of boronic acids or the condensation reaction of boronic acids with diol or ketal forming boroxine or boronate ester^[47,48]; (2) The N–C-linked COFs are commonly divided into imide and ketoenamine-based COFs^[49,50]; (3) The C=C linked COFs belong to a class of porous crystalline frameworks by the sp^2 carbon^[51,52]; (4) COFs with the N=C bond mainly contain triazine-, imine-, hydrazine-, and azine-based functional fragments^[53–55]; (5) The ring-based linked COFs predominantly include phenazine-, dioxin-, imidazole-, benzoxazole- and benzothiazole-based functional fragments^[56–60]. It is worth noting that the aromatic nitrile can undergo the trimerization reaction to form triazine rings, but the synthetic reaction generally occurs at high temperatures under a strong acid system to break the long-range order of skeletal structures. Recently, some highly crystalline CTFs have been synthesized under mild conditions, such as low temperature (< 100 °C) and ambient pressure^[61–63].

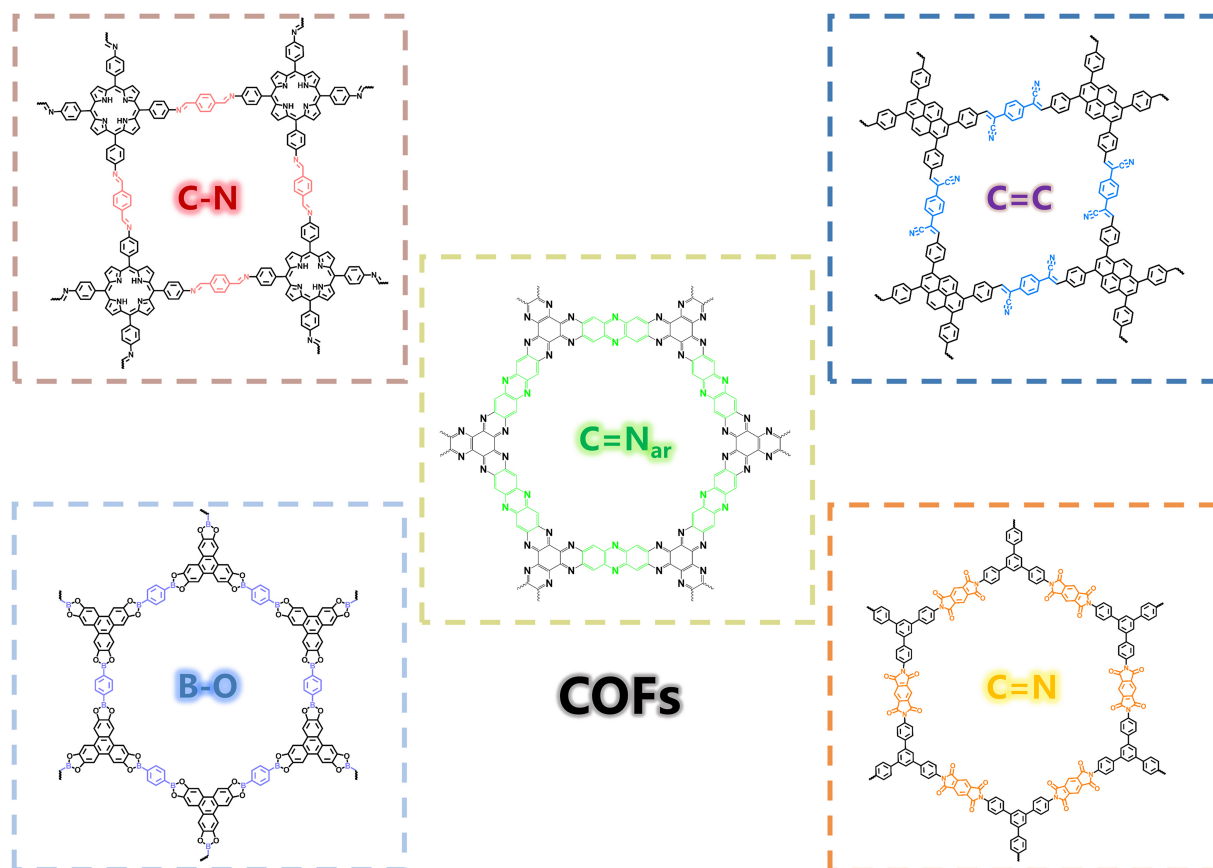


Figure 1. Some commonly used covalent bonds in COFs. COFs: Covalent organic frameworks.

Although crystalline materials have good orderliness, there are still relatively few materials with complete single crystals to determine their fine structures^[64–69]. In general, crystal structures of crystalline POFs are determined through simulation and comparison with powder X-ray diffraction (PXRD) characteristic peaks. This is also a thorny problem that most researchers are trying to solve in the research field of crystalline porous organic materials.

Amorphous porous organic materials

Currently, most of the reported porous COFs have a practical drawback, that is, relatively poor physicochemical stability as compared with amorphous POFs, to limit their use under extreme conditions, which is mainly attributed to the reversible covalent chemistry in crystalline COFs. An increasing number of amorphous porous organic materials, including PAFs, CMPs, and HCPs, have been designed and prepared because of their highly stable and irreversible covalent bonds through Friedel-Crafts alkylation, Suzuki coupling, Yamamoto coupling, Sonogashira-Hagihara cross-coupling, and so on^[70–72]. The specific surface area of porous materials can be analyzed in detail by different adsorption models, including Langmuir theory based on the monomolecular adsorption layer and Brunauer-Emmett-Teller (BET) theory according to the multi-layer adsorption. For example, PAF-1, as a porous polyphenylene framework, was successfully prepared by nickel(0)-catalyzed Yamamoto-type Ullmann cross-coupling [Figure 2A]. PAF-1 not only exhibits excellent stability under extremely harsh conditions, but also has an unprecedented high surface area, including a BET surface area of 5,640 m²·g^{−1} and Langmuir surface area of 7,100 m²·g^{−1}^[73].

Moreover, amorphous porous organic materials can be easily functionalized by the monomer design or post-modification, resulting in the superior targeting function of as-synthesized materials^[74,75]. Recently, PAF-1, as a research mode, has been separately modified by different functional groups, resulting in its excellent

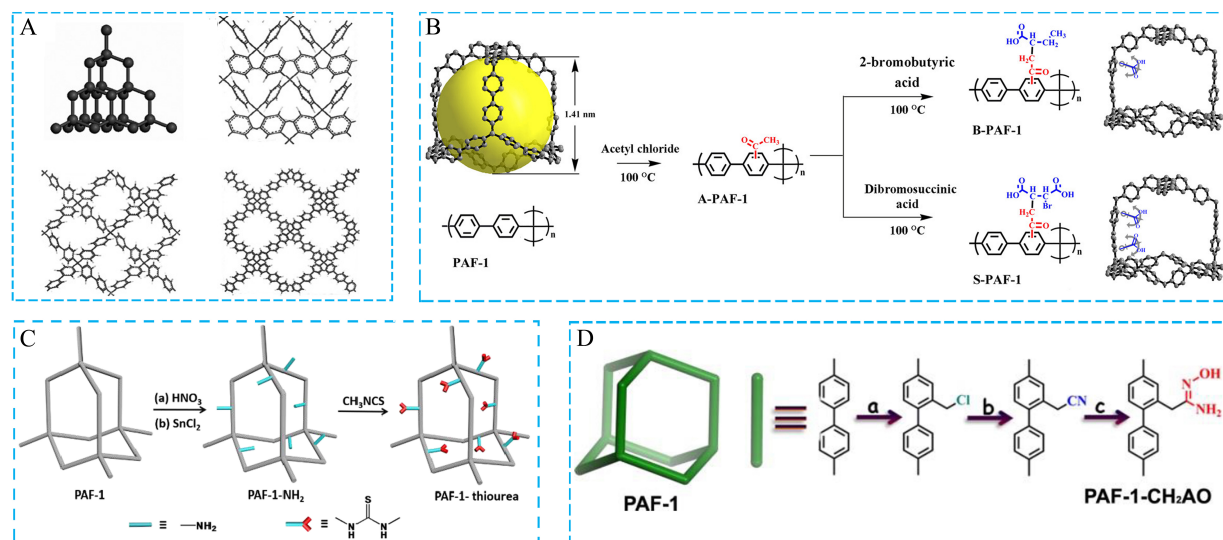


Figure 2. (A) The structure of PAF-1; (B–D) Synthesis schemes for PAF-1 with different functional groups. (A) Adapted with permission^[73]. Copyright 2019, John Wiley and Sons. (B) Adapted with permission^[76]. Copyright 2019, American Chemical Society. (C) Adapted with permission^[77]. Copyright 2020, American Chemical Society. (D) Adapted with permission^[78]. Copyright 2017, American Chemical Society. PAF: Porous aromatic framework.

performance in various applications [Figure 2B–D]^[76–78]. According to their excellent physicochemical stability, rich skeletal structures, and good controllability, amorphous POFs have been widely prepared as a potentially universal platform for numerous application fields.

GREEN SYNTHESIS

Multiple synthesis strategies have been developed to construct porous organic materials, but the commonly used solvent thermal method still needs high temperature and pressure which directly affect the cost, output, and industrial usability of POFs. In order to achieve energy-saving, environmentally friendly, and high-yield preparation, various green synthesis strategies for POFs have been successively explored and developed in recent years.

Room temperature synthesis

Synthesis at room temperature is convenient and economical because it does not require the use of special high or low temperature equipment. This method reduces energy consumption and avoids some temperature-induced side reactions. In addition, the mild synthetic approach can protect the high-temperature sensitive functional groups to construct POFs. Therefore, it offers both energy consumption and operational convenience, leading to its potential application in synthesizing functional POFs^[79–84].

The solvent thermal condition for the preparation of POFs requires the employment of hazardous organic solvents, high reaction temperatures, and intricate systems. For instance, Guo *et al.* described a two-step dissolution precipitation (DP) technique for the synthesis of ketoimines- and imine-linked COFs in an aqueous phase [Figure 3A]^[85]. Using this DP approach, five ketoimine- and two imine-linked COFs were remarkably manufactured in one reaction at room temperature with a reaction time of 5 min. These COFs showed prospective uses in the adsorption of uranyl and iodine, displaying very high crystallinity and porosity. In 2024, Kong *et al.* reported a straightforward and eco-friendly process for room-temperature aqueous solution synthesis of imine bonded-COFs [Figure 3B]^[86]. It is very important to control the reaction rate for the synthesis of crystalline COFs. The reaction reactivity of aldehyde monomers in an aqueous solution was greatly increased by preactivating them with acetic acid (AcOH). The management of reaction equilibrium and product crystallization was made possible by the slightly lower imine production rate and

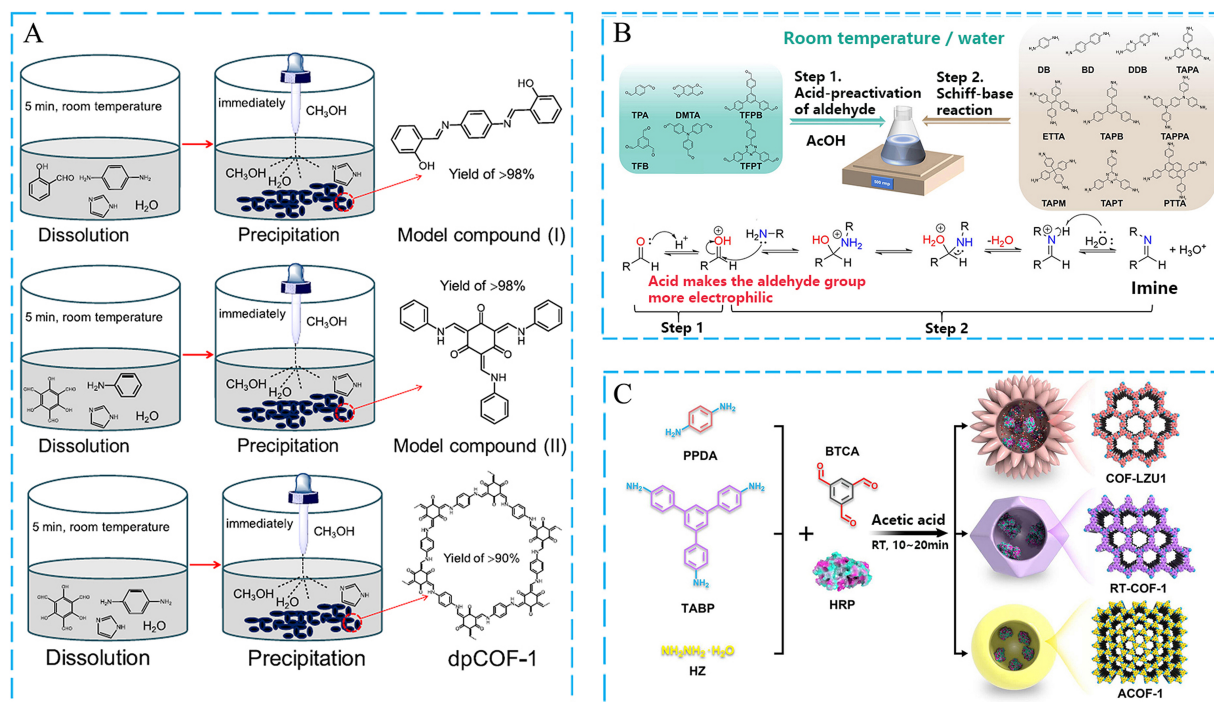


Figure 3. (A) Synthesis of model compounds and dpCOF-1; (B) Schematic depiction of imine-linked COFs and the possible formation mechanism; (C) Schematic diagram of a bio-friendly one-pot synthesis of different HRP-COFs. (A) Adapted with permission^[85]. Copyright 2023, American Chemical Society. (B) Adapted with permission^[86]. Copyright 2024, American Chemical Society. (C) Adapted with permission^[87]. Copyright 2023, John Wiley and Sons. COF: Covalent organic framework; HRP: horseradish peroxidase.

higher imine cleavage rate in an aqueous solution compared to the traditional solvothermal synthesis. Consequently, the crystalline COFs with a large surface area and high yield can be generated in a very short space of time.

In addition, the highly stable and non-metallic properties of COFs make them ideal carriers for enzyme immobilization. Liang *et al.* constructed three types of COFs [benzene-1,3,5-tricarboxaldehyde and p-phenylenediamine co-condensation framework (COF-LZU1), benzene-1,3,5-tricarboxaldehyde and 1,3,5-tris(4-aminophenyl)benzene co-condensation imine-linked framework (RT-COF-1), and benzene-1,3,5-tricarboxaldehyde and hydrazine hydrate co-condensation azine-linked framework (ACOF-1)] using a bio-friendly one-pot synthesis strategy in an aqueous solution at room temperature. COF-LZU1 bound to horseradish peroxidase (HRP) was found to maintain the highest activity [Figure 3C]^[87]. The mild room temperature reaction condition not only reduces the energy consumption and cost, but also can provide an effective synthesis strategy for *in situ* encapsulation of temperature-sensitive substances, such as biomolecules, enzymes, *etc.*, into COFs.

The synthesis of POFs at the liquid-liquid interface at room temperature is a highly anticipated green synthesis method, which can easily and efficiently prepare POF films with adjustable thickness to bring new possibilities to the field of material science^[88,89]. For example, He *et al.* proposed a liquid-liquid IP method to address the challenges in the field of molecular separation [Figure 4A]^[90]. This method restricts the polymerization reaction through the liquid-liquid interface and precisely controls the growth process of COF films, achieving adjustable COF film thickness and providing good flexibility for different applications. This work provides a feasible approach for preparing high-performance COF membranes. Meanwhile, Wu *et al.* adopted a green synthesis strategy of liquid-liquid interfacial polymerization (IP) and successfully synthesized the ethylene-bridged COF membranes with complete sp^2 carbon skeletons at room temperature [Figure 4B]^[91]. The COF nanospheres formed in the initial stage gradually could evolve into self-supporting

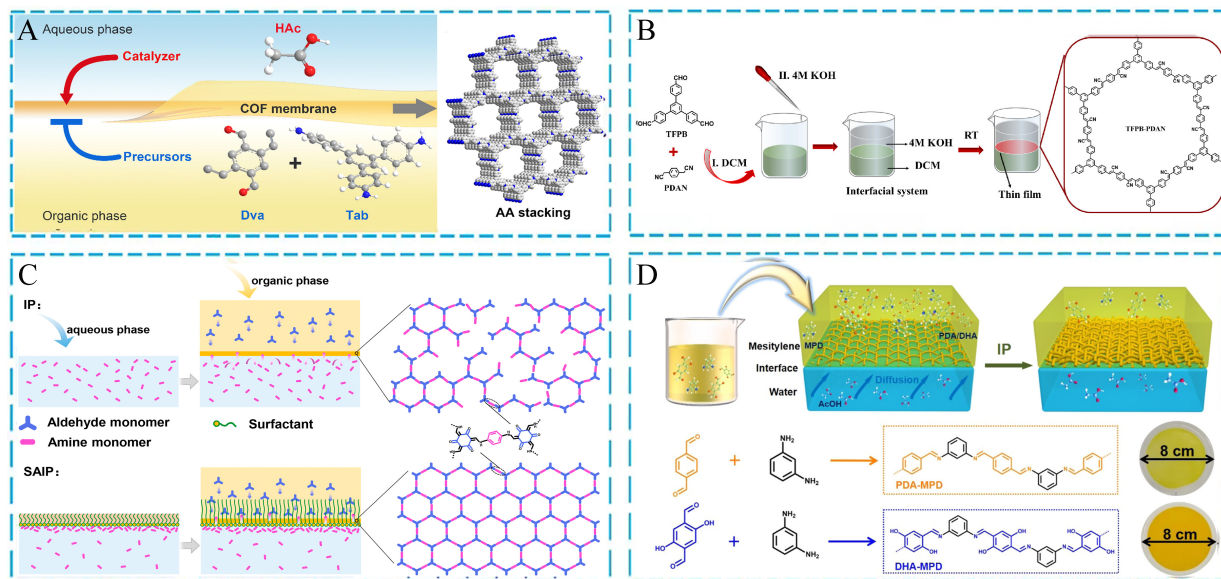


Figure 4. (A) The fabricating process of COF membranes with the AA stacking mode; (B) The vinylene-bridged COF thin films via an interfacial synthesis; (C) SAIP and IP strategies for the synthesis of COF membranes; (D) Interface synthesis diagram and chemical structures of CMP membranes. (A) Adapted with permission^[90]. Copyright 2023, Elsevier. (B) Adapted with permission^[91]. Copyright 2023, American Chemical Society. (C) Adapted with permission^[92]. Copyright 2024, Elsevier. (D) Adapted with permission^[93]. Copyright 2021, American Chemical Society. COF: Covalent organic framework; SAIP: surfactant-assisted interfacial polymerization; IP: interfacial polymerization; CMP: conjugated microporous polymer.

COF thin films with long-range ordered arrangements after covalent self-assembly at the liquid-liquid interface. In addition, Chen *et al.* proposed a room-temperature liquid-liquid interface polymerization method, namely surfactant-assisted IP (SAIP) [Figure 4C]^[92]. By adding surfactants and toluene solvents, the self-assembled chains of zwitterionic surfactants at the interface facilitated the monomer aggregation and pre-assembly to improve their transport at the interface and promote the complete topological growth of COF membranes. This method not only saves polymerization time during the catalytic process, but also enables the preparation of highly crystalline and uniformly porous COF membranes. The interface synthesis strategy at room temperature is applicable to other porous polymers. For instance, Li *et al.* studied a novel method for synthesizing CMPs at room temperature interfaces [Figure 4D]^[93]. Using a strategy based on the Schiff-base reaction, the *in-situ* formation of CMP nanofilms was achieved on porous polymer substrates. During this process, the AcOH migrated from the aqueous phase to the interface, accelerating the aldehyde amine condensation reaction in the oil phase, resulting in the formation of CMP films of terephthalaldehyde (PDA)-m-phenylenediamine (MPD) and 2,5-dihydroxyterephthalaldehyde (DHA)-MPD after 15 min. This strategy provides an enormous potential for the manufacturing of thin film-based electronic and optoelectronic devices.

The lotion polymerization at room temperature, as an important environmental protection synthesis method, has attracted much attention in recent years. This synthetic process was used to construct porous organic materials. For example, Zhang *et al.* proposed a green phase transfer catalyzed lotion polymerization method, which could efficiently and quickly synthesize β -ketoenamine COFs with the controllable morphology [Figure 5A]^[94]. This green method could achieve the fast synthesis of COFs under mild conditions, while avoiding the use of acid catalysts and a large number of organic solvents. The pyridine cationic surfactant not only acts as an emulsifier, but also could be considered an efficient catalyst and shape modifier. This synthetic strategy is fast, simple and green for fabricating COFs. In addition, under mild conditions, Shi *et al.* also conducted a similar work to synthesize porous conjugated polymers with the precise mesoporous size and tunable nanostructure. The synthetic strategy mainly contains the emulsion system of toluene oil/water mixture, the surfactant of triblock copolymer F127, and the precursor of 1,3,

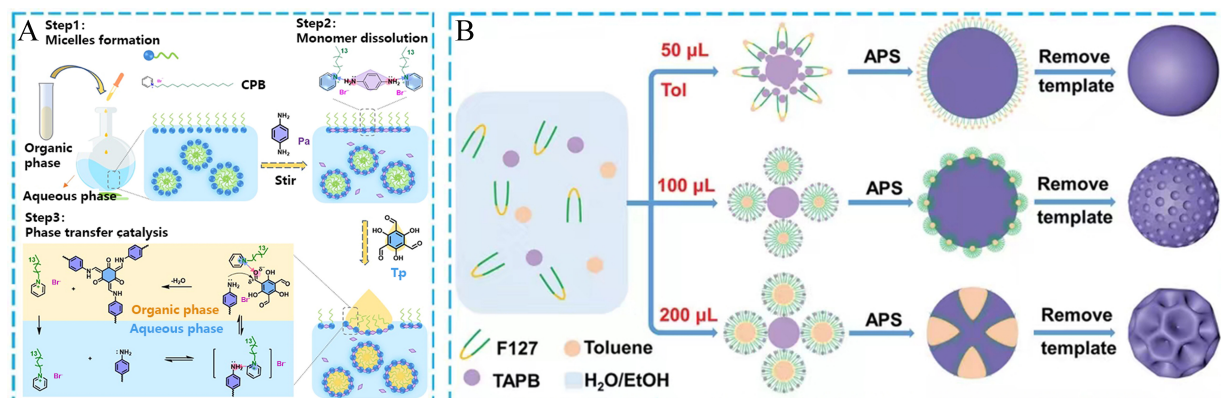


Figure 5. (A) The synthesis description of TpPa-COF; (B) Schematic illustration of π -conjugated porous nanospheres via an emulsion-induced interface assembly strategy. (A) Adapted with permission^[94]. Copyright 2023, American Chemical Society. (B) Adapted with permission^[95]. Copyright 2022, John Wiley and Sons. COF: Covalent organic framework; Tp: 1,3,5-triformylphloroglucinol; TAPB: 1,3,5-tris(4-aminophenyl) benzene; APS: ammonium persulfate.

5-tris(4-aminophenyl) benzene (TAPB) [Figure 5B]^[95]. The TAPB monomers in an aqueous solution were prone to self-aggregation phenomena at room temperature by the oxidative polymerization of aromatic multi-amines catalyzed by the ammonium persulfate (APS) oxidant. Notably, the mild condition could offer good compatibility with the soft-template self-assembly strategy, which was easily removed while ensuring no damage to the targeted materials. Hence, a series of uniform π -CMPs with different pore diameters were obtained through this one-pot operation.

According to the above reports, room temperature synthesis is considered as a green approach to construct porous organic materials. The mild reaction condition provides an available approach to control the morphology and size of porous materials. However, room temperature conditions may lead to poor solubility of organic monomers to limit their application in the preparation of POFs. In addition, most reports still focus on porous organic materials formed by reversible covalent bonds, and the applicability of non-reversible covalent bond-based porous materials needs further exploration and certification.

Green solvent synthesis

Except for some specific synthesis methods, most porous organic materials require solvents during the synthesis process. Organic solvents can dissolve various organic monomers to provide a molecular-level reaction environment. Meanwhile, the high boiling point of organic solvents can allow the synthetic reactions to occur at high temperatures. However, organic solvents are expensive and toxic, which also need to be solved from the perspective of green environmental protection. In the realm of green chemistry, numerous researchers have put forth a variety of creative techniques and strategies to prepare POFs via green solvents. For instance, Zhao *et al.* successfully created high crystallinity COF materials with rich pore structures in a short reaction time by utilizing the ultrasonic chemical synthesis method and green solvents [Figure 6A]^[96]. These COF materials included two novel structural COFs and seven previously described COFs. This synthetic approach may be utilized to create three-dimensional and two-dimensional COFs with suspension functionalization. Ultrasound chemistry, in conjunction with green solvents, provides a practical way to quickly synthesize crystalline POFs.

On the other hand, the aqueous reaction system is thought of as an available green synthesis method to construct POFs, especially two-dimensional thin films. Recently, Wang *et al.* made a breakthrough in the construction of membranes in non-organic solvent systems [Figure 6B]^[97]. The aqueous two-phase system (ATPS) approach was used to prepare COF membranes from a green chemistry perspective. In order to create a dual aqueous system, the organic monomers of COFs were dissolved in the lower aqueous phase of

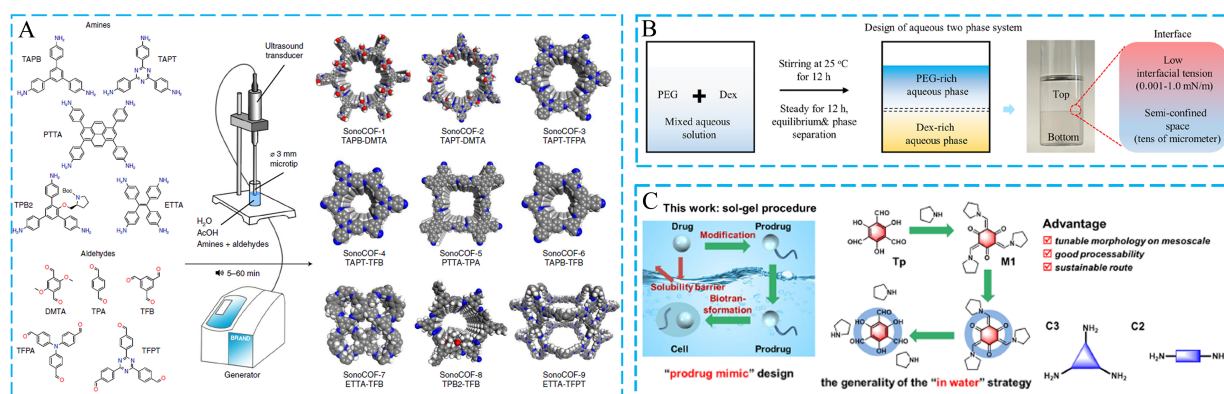


Figure 6. (A) The sonochemical synthesis for crystalline COFs; (B) The ATPS approach for COF membranes; (C) The “in-water” strategy is inspired by the “prodrug mimic” design methodology. (A) Adapted with permission^[96]. Copyright 2022, Springer Nature. (B) Adapted with permission^[97]. Copyright 2022, Springer Nature. (C) Adapted with permission^[98]. Copyright 2023, American Chemical Society. COF: Covalent organic framework; ATPS: aqueous two-phase system; Dex: dextran; PEG: polyethylene glycol.

dextran (Dex) and the upper aqueous phase of polyethylene glycol (PEG), respectively. IP was a good platform to create COF membranes with varying levels of crystallinity. The significant result showed that the continuous COF membranes throughout the film-forming process depended critically on the proper water-water interface tension. This study could be applied to produce premium membrane materials, serving as an environmentally friendly membrane manufacturing technique. Additionally, Hu *et al.* were able to create COF colloidal dispersions by adding polar groups, which increased the water solubility of aldehydes. They demonstrated the overall procedure for synthesizing processable COFs in water via the sol-gel technique [Figure 6C]^[98]. In addition to offering significant insights for the sustainable preparation in the realm of green chemistry, this proposed sol-gel strategy could be applied for shaping and synthesizing β -ketoenamine-linked two-dimensional COFs.

Besides the common COFs formed by the dynamic aldehyde-amine condensation, ethylene-linked COFs have attracted lots of attention due to their outstanding stability. In recent years, some researchers have focused on the study of the crystallinity and ionic properties of olefin- or vinylene-linked COFs via green synthetic approaches. A typical example was reported by Zhang *et al.* in 2023. In this work, the authors utilized the DMAP catalyst and hydrothermal conditions to successfully synthesize highly crystalline and robust zwitterionic vinylene-linked COFs (ZVCOFs) from the pre-designed zwitterionic building blocks [Figure 7A]^[99]. For the hydrothermal strategy, water molecules reduced the activation energy barrier to improve the reaction reversibility. Meanwhile, the introduced water facilitated the hydration of zwitterionic sites, promoted ordered layered arrangement, and provided an effective pathway for the crystallization of ZVCOFs. These findings not only provide new ideas and methods for the synthesis of ZVCOFs, but also have certain research value for a deeper understanding of the water role in the synthesis process. Another important work was reported by Yang *et al.* [Figure 7B]^[100]. Vinylene-linked cationic two-dimensional polymers thin films (namely V-C2DP-1 and V-C2DP-2) were prepared on the water surface by employing the Knoevenagel polycondensation reaction in conjunction with a sodium oleyl sulfate (SOS) surfactant. The air/water interface not only effectively inhibited the out-of-plane movement of the organic molecules, but also enhanced the nucleophilic ability of the reaction intermediates. These films were appropriate for usage as anionic selective electrode coatings due to their vast area, tunable thickness, and great chemical stability. This work develops a green approach to construct highly stable and oriented V-C2DP thin films, and has an important potential application in the next generation of energy devices.

Furthermore, some reports have been focused on the synthesis of porous organic materials in water systems^[101-104]. Many researches show that green solvent synthesis is considered as a feasible approach to

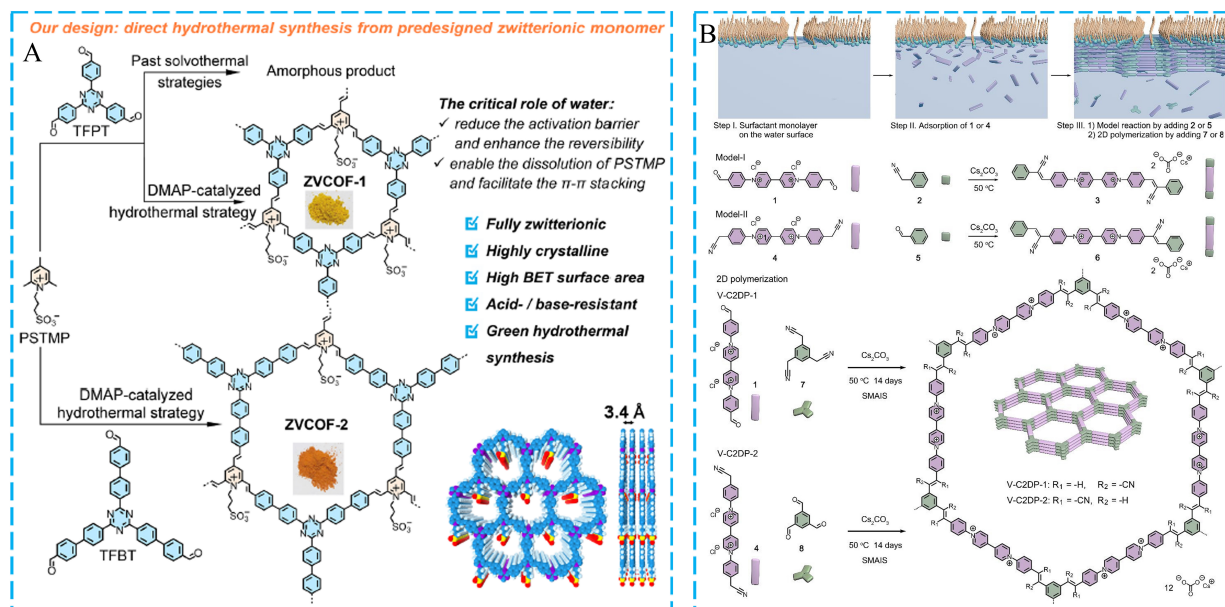


Figure 7. (A) Schematic illustration for constructing ZVCOFs; (B) The synthetic process of V-C2DPs through the SMAIS method. (A) Adapted with permission^[99]. Copyright 2023, American Chemical Society. (B) Adapted with permission^[100]. Copyright 2024, John Wiley and Sons. COF: Covalent organic framework; DMAP: 4-dimethylaminopyridine; ZVCOF: zwitterionic vinylene-linked COF; V-C2DPs: vinylene-linked two-dimensional polymer; SMAIS: surfactant-monolayer assisted interfacial synthesis.

construct porous materials. Obviously, water is the most commonly used and ideal green solvent. However, most organic molecules have low solubility in water, which causes significant challenges for the fabrication of POFs in aqueous systems. Meanwhile, the correlational research on porous materials linked by different covalent bonds still needs to be further investigated and explored.

Solvent-free synthesis

Solvent-free synthesis can avoid the use and removal of organic solvents during the preparation of porous organic materials. From the perspectives of energy conservation, environmental protection, ease of operation, and cost-effectiveness, the solvent-free strategy is highly appealing and offers potential application value for large-scale POF production.

Recently, the use of molten salts as the reaction solvent, structure-directing agent, and catalyst has been proven to be an efficient and green method to synthesize POFs. Especially, CTFs, as a class of porous organic materials, are commonly prepared by the cyclotrimerization of aromatic nitriles in the molten $ZnCl_2$ salt at high temperatures^[105–110]. Metal salts are considered as Lewis acid sites to catalyze the trimerization reaction, and the molten reaction system can accelerate the mass transfer process. For example, Rangaraj *et al.* prepared phosphonitrilic core-based CTFs (namely Pz-CTFs) by the molten $ZnCl_2$ in the temperature range from 400 to 600 °C [Figure 8A]^[111]. Different contents of HCPz and $ZnCl_2$ were separately mixed into a quartz ampoule and heated at a variety of temperatures to obtain six Pz-CTFs samples. The rigid phosphonitrilic unit offered rigidity and enhanced the electron-rich centers in the framework. Moreover, the hexacyano group in the precursors increased the interconnected crosslinking density and the thermal stability of Pz-CTFs. Although Pz-CTFs were amorphous porous materials, Pz-CTF-6 (monomer/ $ZnCl_2$ molar ratio of 1:10) showed a high surface area and excellent CO_2 adsorption with good selectivity and regeneration. Notably, when the cyclotrimerization took place at above 300 °C, the undesired carbonization decreased the CTF crystallinity and caused different structural defects. In order to overcome these problems, Lan *et al.* reported an ionothermal synthesis method for CTF-based photocatalysts using a ternary NaCl-KCl- $ZnCl_2$ eutectic salt (ES) mixture with a melting point of approximately 200 °C. This temperature was lower than the melting point of pure $ZnCl_2$, thus providing milder salt-melt conditions. The mild reaction

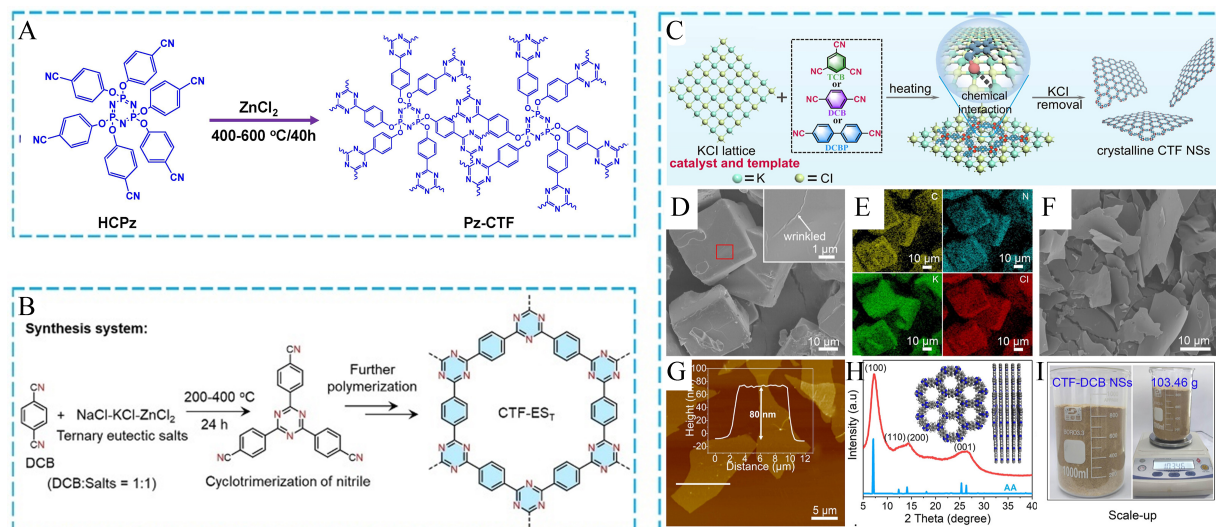


Figure 8. (A) Schematic diagram of the preparation process of Pz-CTFs; (B) Ionothermal synthetic CTF-based photocatalysts via a ternary NaCl-KCl-ZnCl₂ system; (C) The polymerization reaction for CTFs by the KCl-catalytic approach; (D) SEM and (E) EDS element mappings of KCl nanoparticles coated by CTF-DCB NSs; (F) SEM, (G) AFM, and (H) PXRD of CTF-DCB NSs; (I) Large-scale preparation of CTF-DCB NSs. (A) Adapted with permission^[111]. Copyright 2022, Elsevier. (B) Adapted with permission^[112]. Copyright 2022, John Wiley and Sons. (C-I) Adapted with permission^[113]. Copyright 2023, American Chemical Society. Pz-CTF: Phosphonitrilic core covalent triazine framework; HCPz: hexakis(oxy)hexabenzonitrile phosphazene; SEM: scanning electron microscopy; EDS: energy-dispersive spectrometry; CTF-DCB NS: covalent triazine framework-dicyanobenzene nanosheet; AFM: atomic force microscopy; PXRD: powder X-ray diffraction.

condition facilitated the polycondensation process to avoid the carbonization of the polymeric backbone, so the as-synthesized CTF-ES200 obtained at 200 °C exhibited few structural defects and high crystallinity with remarkable photocatalytic performance for hydrogen evolution [Figure 8B]^[112]. Moreover, there is an urgent need for the scalable and eco-friendly green synthesis of crystalline two-dimensional CTF nanosheets (NSs), which remains a huge and challenging fundamental research. Excitingly, Wang *et al.* developed a feasible and solvent-free KCl-catalyzed strategy for the large-scale production of crystalline CTF NSs through two-dimensional polymerization and salt removal processes [Figure 8C]^[113]. Scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS) mapping images of the CTF-1,4-dicyanobenzene (DCB) NS-coated KCl illustrated that CTF-DCB NSs were successfully prepared on the surface of KCl nanoparticles [Figure 8D and E]. The as-synthesized CTF-DCB NSs after the water washing treatment showed a smooth surface with an ~80 nm film thickness by SEM and atomic force microscopy (AFM) images [Figure 8F and G]. The strong PXRD reflection peaks in Figure 8H confirmed the ordered skeleton of CTF-DCB NSs. As seen in Figure 8I, the large-scale synthesis of crystalline CTF-DCB NSs was easy to achieve via this synthetic process. In addition, KCl is necessary for the cyclotrimerization reaction in the construction of crystalline CTF-DCB NSs via a series of comparative experiments.

To further overcome the shortcomings of molten metal salts, different catalysts have been used to prepare CTFs in recent years. One reported catalyst is P₂O₅, which can catalyze the trimerization reaction of aromatic primary amide groups to *s*-triazine rings. As seen in Figure 9A and B, a two-dimensional stacked covalent triazine-based framework (*p*CTF-1) with a large surface area was synthesized via the P₂O₅-catalyzed dehydration condensation of terephthalamide (TA) molecules^[114]. This porous material exhibited high CO₂ and H₂ sorption abilities. Another research team prepared *p*CTF by P₂O₅ to detect NH₃ gas at room temperature^[115]. Both reports demonstrated that aromatic amide and nitrile compounds could be catalyzed by P₂O₅ at high temperatures to produce porous CTFs. Meanwhile, H₆P₄O₁₃ as a commonly used polyphosphoric acid was applied to catalyze the nitrile trimerization reaction, leading to the formation of four two-dimensional crystalline CTFs as confirmed by PXRD patterns [Figure 9C-G]^[116]. Especially, the high crystallinity of as-synthesized CTFs endowed them with large surface areas in the range of 794-

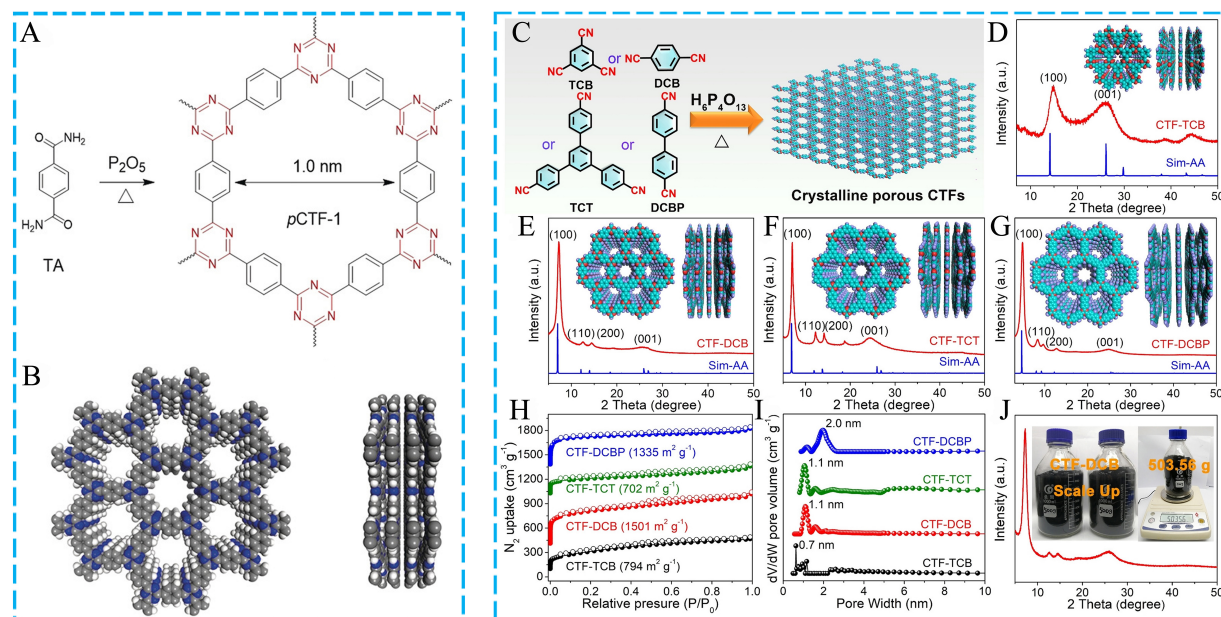


Figure 9. (A) The P_2O_5 -catalyzed dehydration condensation for the synthesis of pCTF-1; (B) The crystal structure of pCTF-1; (C) The synthetic strategy of crystalline CTFs by $H_6P_4O_{13}$; (D-G) PXRD patterns of different as-synthesized CTFs; (H) N_2 sorption isotherms at 77 K and (I) pore size distributions of four CTFs; (J) The large-scale preparation of CTF-DCB. (A and B) Adapted with permission^[114]. Copyright 2018, John Wiley and Sons. (C-J) Adapted with permission^[116]. Copyright 2022, John Wiley and Sons. TA: Terephthalamide; DCB: 1,4-dicyanobenzene; CTF: covalent triazine framework; TCB: 1,3,5-tris(*N*-carbazolyl)benzene; PXRD: powder X-ray diffraction.

1,335 $m^2 \cdot g^{-1}$ and the pore size distribution from 0.7 to 2.0 nm [Figure 9H and I]. Thanks to the convenience and environmental friendliness of this synthesis approach, the low-cost DCB monomer, as a reaction mode, was used to prepare the highly crystalline CTF-DCB at the kilogram level [Figure 9J]. Hence, the metal/solvent-free $H_6P_4O_{13}$ system is a feasible and green synthetic approach for the large-scale fabrication of highly crystalline porous CTFs.

Furthermore, it is still a formidable challenge for the large-scale and low-cost synthesis of POFs to meet the industrial demand. Recently, Zhang *et al.* have focused on the development of novel green strategies to prepare COFs in large quantities. One example was reported to produce COFs with highly ordered structures^[117]. In this work, the authors attempted to efficiently prepare collidine-based COFs with olefin linkages via a green melt polymerization strategy of PDA and 2,4,6-collidine [Figure 10A]. Referring to the research from Wang *et al.*, benzoic anhydride was considered as a potential molecule to balance crystallization and polymerization, leading to the generation of COFs with outstanding crystallinity. As a comparison, no product was generated using the traditional solvothermal method, and an amorphous polymer was found through the direct reaction without benzoic anhydride and its derivatives. It is worth noting that over one kilogram of COFs could be acquired at low costs, indicating the enormous potential application value in the industrial field. On the other hand, this research group further proposed an organic flux-mediated synthesis to construct highly crystalline irreversible-linked COFs, which showed more outstanding application potentials than the reversible-linked COFs due to the higher stability and structural robustness of the irreversible-linked COFs^[118]. Nevertheless, feasible and green synthetic methods are lacking for the irreversible-linked COFs. As seen in Figure 10B, the acidic molecules were used as modulators and reactive fluxes to prepare imide-linked COFs. The possible catalytic mechanism mainly contains two steps. The amide precursors were obtained by the reaction between benzoic acid and triamine, leading to good solubility in the benzoic acid flux. Another organic monomer could slowly replace the previously formed precursors through the covalent bond conversion from amide to imide, resulting in the generation of the targeted imide-linked COFs. The same COFs were prepared by the traditional solvothermal approach, which

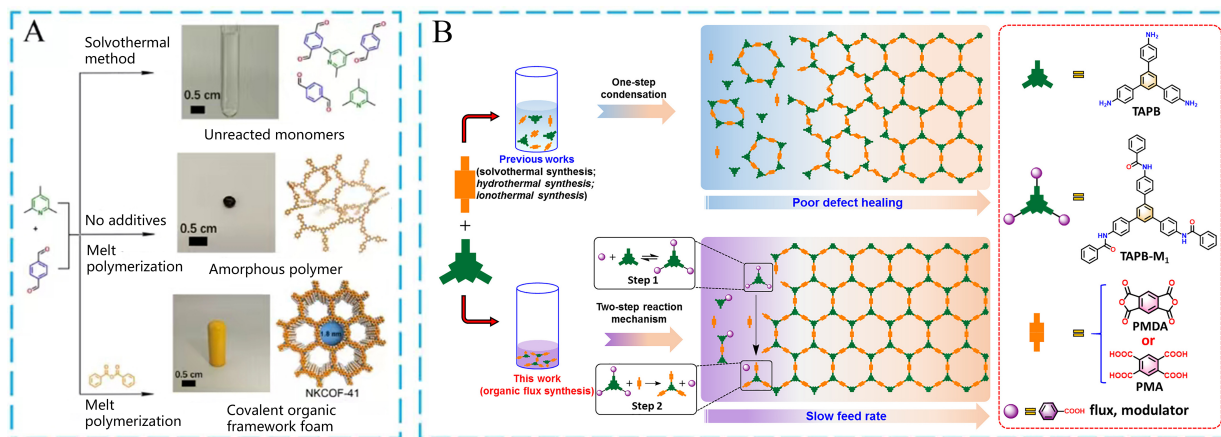


Figure 10. (A) Synthetic strategies, optics pictures, and simulated structures of as-synthesized samples using different strategies; (B) Schematic diagram of reaction routes and possible mechanisms. (A) Adapted with permission^[117]. Copyright 2022, John Wiley and Sons. (B) Adapted with permission^[118]. Copyright 2023, Elsevier. COF: Covalent organic framework; TAPB: 1,3,5-tris(4-aminophenyl) benzene.

were used as comparative materials. What is even more exciting is that the flu-synthesized COFs exhibited larger surface areas and higher crystallinity. The flux synthesis provides a convenient gram-scale synthetic strategy to obtain crystalline irreversible-linkage COFs.

Solvent-free synthesis is an environmentally friendly method, which can utilize different catalytic systems, such as metal salts, P_2O_5 , $H_6P_4O_{13}$, and benzoic anhydride, to realize the control preparation of porous organic materials. Especially, the synthetic approach can enhance the stability and crystallinity of POFs, even for irreversible covalent bonds-based porous organic skeletons. However, this method is usually processed under high temperatures to trigger thermal decomposition or carbonization of the monomer. Developing more catalytic systems for the preparation of POFs under mild conditions remains a great challenge.

Mechanochemical synthesis

Mechanochemical synthesis is a simple, economical and environmentally friendly method. During this process, the reaction monomers are put into a mortar or machine at room or low temperature with a little or no solvent via different rotational speeds and reaction times^[119–121]. The mechanical force can be utilized as the main energy source for producing POFs.

Recently, some research groups have focused on the design and synthesis of POFs via the mechanochemical approach^[122–124]. The main type of COFs is almost prepared by the aldehyde-amine Schiff-base condensation. For example, Shinde *et al.* prepared bipyridine functionalized COFs with permanent porosity, crystallinity and strong acid-base stability by a liquid-assisted mechanochemical route [Figure 11A]^[122]. The mechanochemically prepared COFs possessed less porous and more compact pellets, which could be used as a solid-state electrolyte with higher conductivity and more stable open circuit voltage. Another luminescent COF was reported by Liu *et al.*, who successfully prepared COF-TpMA (MC) via the low-cost mechanochemical synthesis of triformylphloroglucinol (Tp) and melamine (MA) monomers [Figure 11B]^[123]. Noticeably, the mechanochromic luminescence properties of COF-TpMA (MC) showed that the original intermolecular interaction and electron transport channel could be destroyed by the mechanical stimulation. As a result, COF-TpMA (MC) was a good luminescence sensing material to detect $\cdot OH$ in living systems with high sensitivity and selectivity. In addition to the direct synthesis of COFs, the external surface post-modification of pre-synthesized materials could be carried out via the convenient ball milling process. In 2024, Zhang *et al.* successfully synthesized a thiadiazole-functionalized COF-F (Thdz@COF-F) by the combination of solvothermal and ball milling approaches [Figure 11C]^[124]. The solvothermally generated COF-F was aldehyde terminated by controlling the suitable proportion of 4,4',4''-(1,

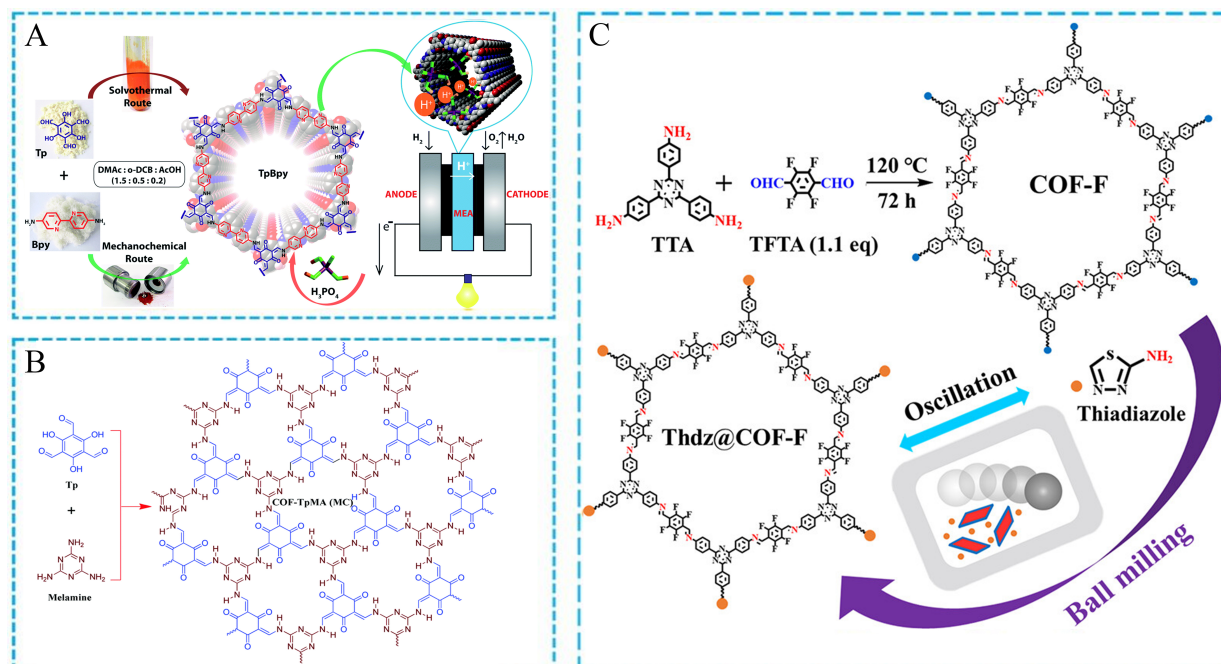


Figure 11. (A) Schematic representation of the TpBpy COF as a solid-state electrolyte; (B) Chemical structures of monomers and COF-TpMA (MC); (C) The preparation process of Thdz@COF-F. (A) Adapted with permission^[122]. Copyright 2016, Royal Society of Chemistry. (B) Adapted with permission^[123]. Copyright 2019, Royal Society of Chemistry. (C) Adapted with permission^[124]. Copyright 2024, American Chemical Society. COF: Covalent organic framework; Tp: 1,3,5-triformylphloroglucinol; MA: melamine; TTA: 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline; TFTA: 2,3,5,6-tetrafluoroterephthalaldehyde.

3,5-triazine-2,4,6-triyl)trianiline (TTA) and 2,3,5,6-tetrafluoroterephthalaldehyde (TFTA). The active aldehyde group of COF-F could react with the amino thiadiazole through a convenient mechanochemical reaction. Ball milling played a crucial role in accelerating the Schiff base reaction mainly owe to the impact and shear force, achieving the Schiff base reaction of an aldehyde group on the COF skeleton and the amino group of thiadiazole. The as-synthesized Thdz@COF-F exhibited outstanding lubrication performance for reducing friction and wear.

Moreover, two porous organic materials [TMCPD (MC) and TMCBD (MC), with TMCPD (MC) synthesized from *p*-phenylenediamine and 1,3,5-benzenetricarbonyl chloride and TMCBD (MC) derived from benzidine and 1,3,5-benzenetricarbonyl chloride using mechanochemical methods] based on the secondary amide linkage were obtained by a solvent-free, fast, and room temperature mechanochemical synthesis [Figure 12A]^[125]. The organic coupling reaction of amine and acid chloride easily occurred in the presence of triethylamine as an acid binding agent. The flexible amide linkage made the dynamic skeleton of POFs with multiple hydrogen bond donor and acceptor sites. Another similar work was reported by Li *et al.* Two COFs, COF-TP and COF-TE, were separately constructed by the polymerization reaction of 1,3,5-trimesoyl chloride and diamine (*p*-phenylenediamine or ethylenediamine) through an environmentally friendly and efficient ball-milling approach [Figure 12B]^[126]. The porous COFs showed lamellar structures with the amide functional groups to capture Pb(II) cations. In addition, another meaningful work was reported by Jie *et al.* A novel porous organic material with hydrophenazine linkage (namely MHP-P5Q) was mechanochemically synthesized by the reaction between triptycenehexamine and pillar[5]quinone (P5Q) without any solvents and catalysts [Figure 12C]^[127]. The microporous structure and the rigid pillar[5]arene cavity could provide multiple interactions for the efficient and rapid capture of CH₃I. This work expands the application of mechanochemical synthesis in the field of porous organic materials based on supramolecular macrocycles.

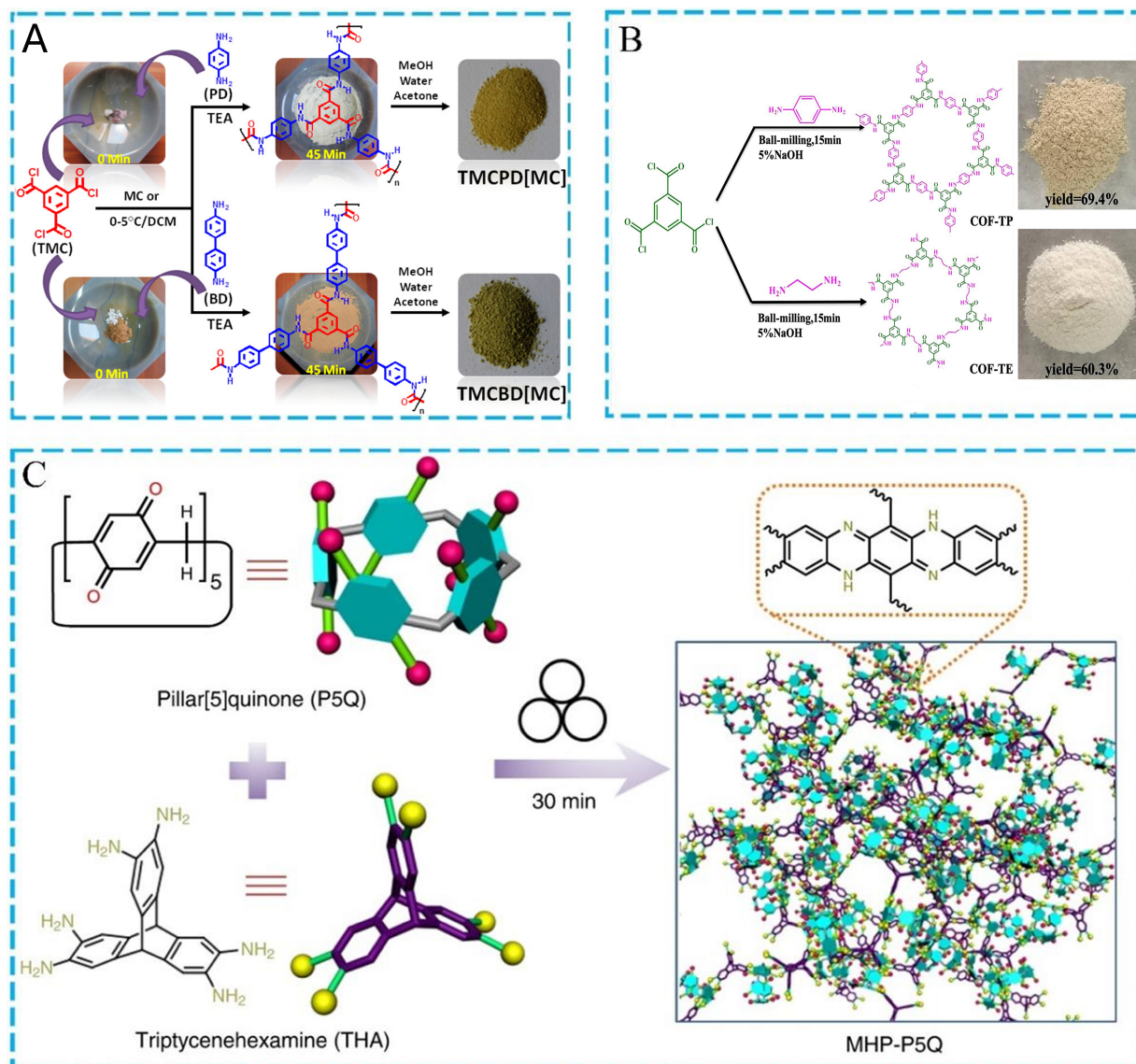


Figure 12. Mechanochemical synthesis of (A) amide-based TMCPD and TMCBD, (B) COF-TP and COF-TE, and (C) MHP-P5Q. (A) Adapted with permission^[125]. Copyright 2014, American Chemical Society. (B) Adapted with permission^[126]. Copyright 2019, Elsevier. (C) Adapted with permission^[127]. Copyright 2020, Springer Nature. COF: Covalent organic framework; P5Q: pillar[5]quinone.

Mechanochemical Friedel-Crafts alkylation is also a commonly used polymerization coupling reaction for the fabrication of POFs. Troschke *et al.* synthesized a series of porous CTFs through the mechanochemical synthesis based on a Friedel-Crafts alkylation reaction mechanism^[128]. The easily available MA chloride as a triazine node reacted with different electron-rich aromatic compounds [Figure 13A]. Carbazole and cyanuric chloride were mixed with each other in the presence of AlCl_3 as an activating reagent and ZnCl_2 as a bulking agent, leading to the synthesis of the porous carbazole-CTF with a large specific surface area after ball milling for 1 h. This study offers a solvent-free, time-efficient, and scalable production of CTFs via the mechanochemical synthesis. Another type of polymerization is monomer self-polymerization or cross-coupling in solvents. For example, Chen *et al.* synthesized multiple PAFs via the FeCl_3 -promoted mechanical coupling reaction using *p*-terphenyl and *o*-terphenyl as reaction monomers [Figure 13B]^[129]. The introduced formaldehyde dimethyl acetal (FDA) could form the C–O bond-linked PAFs. These as-synthesized porous PAFs could adsorb and separate C_2 hydrocarbons. Another similar work was reported by Krusenbaum *et al.*^[130]. As a commonly used organic aromatic monomer, 1,3,5-triphenylbenzene (TPB) could respectively react with two organochloride crosslinking agents, CH_2Cl_2 and CHCl_3 , via the mechanochemical

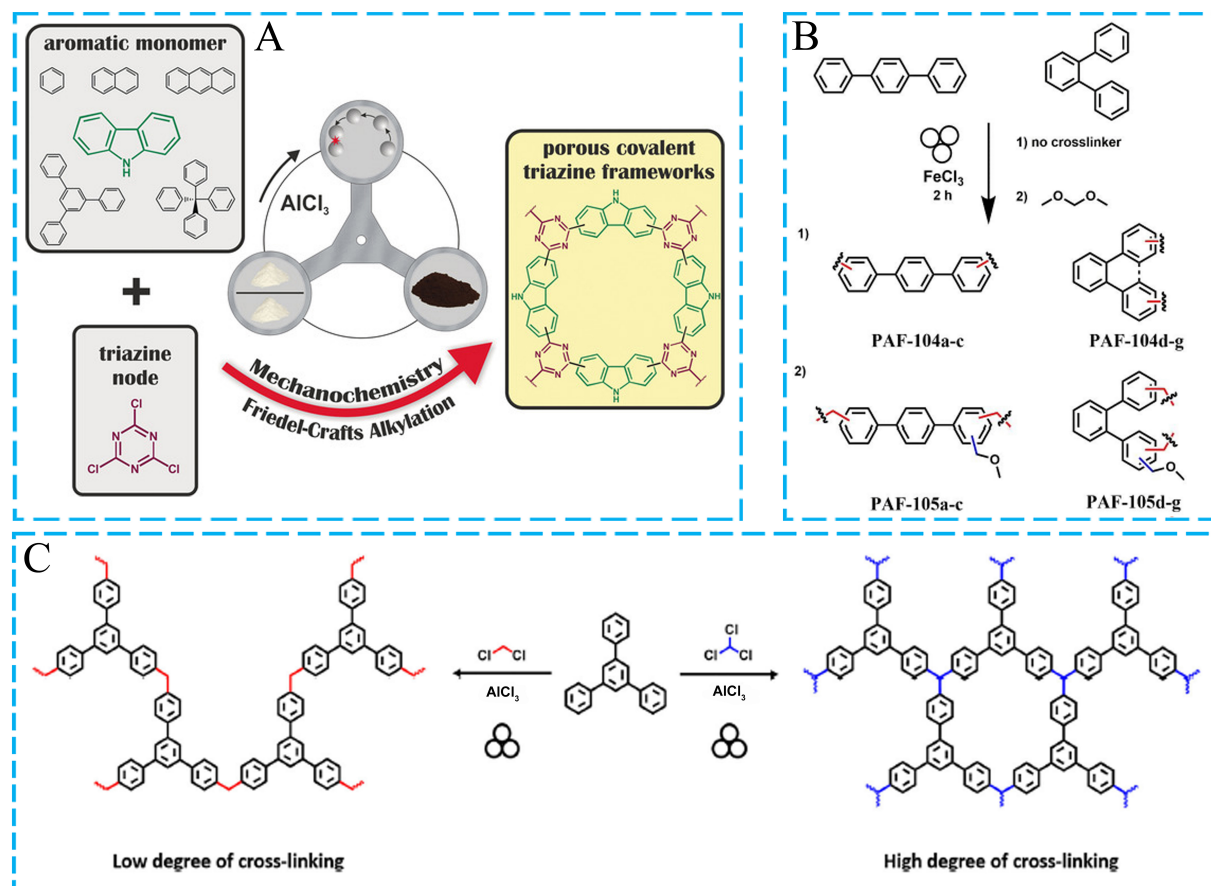


Figure 13. (A) Mechanochemical synthesis of CTFs by melamine chloride and various aromatic monomers; (B) The mechanically synthetic processes of PAF-104 and PAF-105 via the FeCl_3 -promoted reaction; (C) The mechanochemical Friedel-Crafts alkylation of TPB and two organochloride crosslinking agents. (A) Adapted with permission^[128]. Copyright 2017, John Wiley and Sons. (B) Adapted with permission^[129]. Copyright 2022, Royal Society of Chemistry. (C) Adapted with permission^[130]. Copyright 2022, John Wiley and Sons. CTFs: Covalent triazine frameworks; PAF: porous aromatic framework; TPB: 1,3,5-triphenylbenzene.

Friedel-Crafts alkylation [Figure 13C]. The CH_2Cl_2 -linked polymer was a flexible porous structure with low-degree polymerization, but the CHCl_3 -linked porous organic polymer showed a highly crosslinked rigid skeleton with a larger surface area. Other similar works were reported by other groups^[131–133]. Hence, the mechanochemical Friedel-Crafts alkylation provides a versatile tool to generate porous organic materials.

Furthermore, ionic porous organic polymers can be synthesized by the mechanochemical method. The targeted functional ionic POFs are prepared via the solid grinding coupling reaction of ionic organic blocks. For instance, Zhang *et al.* prepared cation-functionalized charged porous polymers (CPPs) by a dibenzodioxane-forming reaction between the contorted 5,5,6,6-tetrahydroxy-3,3,3,3-tetramethyl-1,1'-spirobisindane (TTSBI) and fluorine-activated ionic monomers. The mild, environmentally friendly, and highly efficient mechanochemical method was carried out to produce cationic CPPs [Figure 14A]^[134]. Compared with the traditional solvothermal synthesis method, the mechanochemical grinding approach can quickly complete the polymerization process after 60–90 min and reduce the condensation reaction temperature. Another class of porous ionic polymers (PIPs) was reported by Hou *et al.*^[135]. As illustrated in Figure 14B, different neutral organic monomers containing pyridine or benzyl bromide fragments were used for the mechanical grinding synthesis of various cationic PIPs via the Menshutkin coupling reaction. NaBr, as a salt template, was rationally introduced in the reaction system, which was also easy to reuse for reducing the environmental pollution. The above two examples prove that the green mechanical synthesis is a useful method to construct ionic porous organic materials.

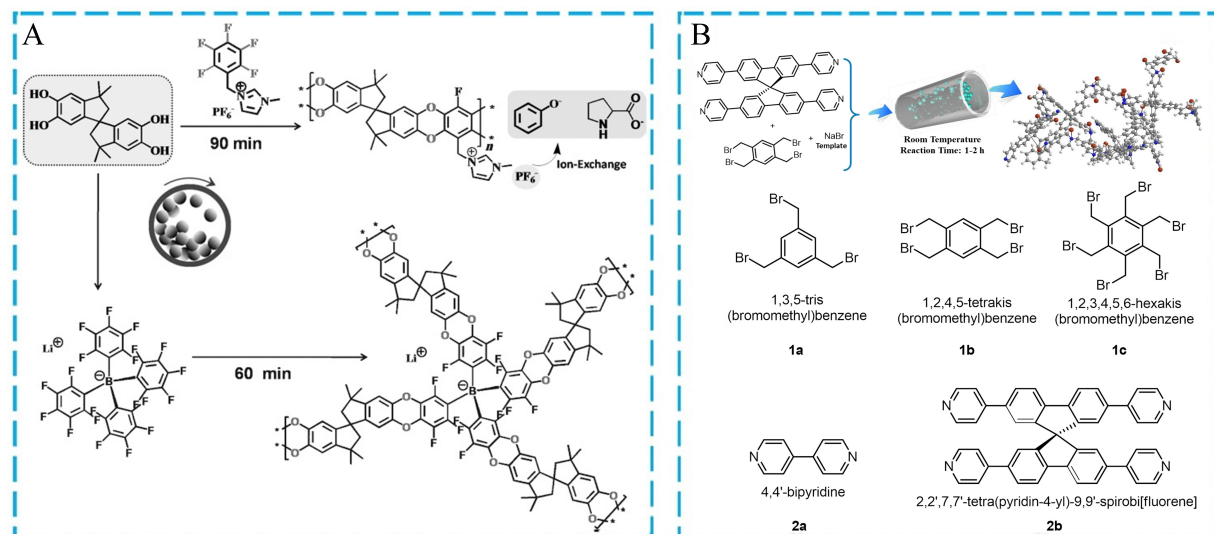


Figure 14. The mechanochemical synthetic illustration of (A) CPPs and (B) PIPs. (A) Adapted with permission^[134]. Copyright 2015, John Wiley and Sons. (B) Adapted with permission^[135]. Copyright 2021, John Wiley and Sons. CPP: Charged porous polymer; PIP: porous ionic polymer.

The mechanochemical process has many advantages, including being solvent-free, operating at low temperatures, enabling large-scale production, and allowing fast reactions, making it a highly promising method in the preparation of POFs. For different catalytic reactions, it takes considerable time to determine the mechanical synthetic conditions, such as the addition of catalysts and other excipients. Therefore, the use of mechanochemical construction of porous organic materials still needs a lot of research in the future.

Electrochemical synthesis

Electrochemical synthesis technology features environmental friendliness, high efficiency, low emissions, and precise controllability. The controllable energy input from the electrode offers an opportunity to manipulate the chemical reaction in a pre-designed manner and in a confined space. In recent years, various materials, such as COFs, CMPs and PAFs, have been successfully fabricated by the electrochemical synthesis, exhibiting high fabrication efficiency^[136–138].

Electrochemical synthesis of COFs has been reported by different research groups. In 2023, Shirokura *et al.* synthesized a TAPB-PDA COF film by an electrochemical synthesis method [Figure 15A]^[139]. In this work, electrochemical oxidation of 1,2-diphenylhydrazine (DPH) produced electrogenerated acid (EGA) at an electrode surface, which could act as an effective Brønsted acid catalyst to improve imine bond formation from the corresponding amine and aldehyde monomers. Simultaneously, it provided the corresponding COF film deposited on the electrode surface. The as-synthesized COFs not only possessed high crystallinity and abundant pores, but also exhibited the controlled film thickness through using the potential-sweep method [Figure 15B]. In addition, Wang *et al.* created an electrochemical IP technique for three distinct ultrathin COF membranes in the same year. The aldehyde monomer (Tp) and the amine monomer (Pa) were dissolved in methanol, which could migrate to the cathode under the control of voltage and current [Figure 15C]^[140]. The rapidly accelerating polymerization-crystallization process of COFs could be realized by the electrochemical deprotonation reaction and the electric field migration behavior. SEM and transmission electron microscopy (TEM) images were measured to observe the TpPa membrane on the polyacrylonitrile (PAN) substrate with the increased electrochemical time [Figure 15D–O]. With the extension of electrochemical time to 4 h, the thickness of the as-synthesized TpPa membrane increased to the maximum value of 85 nm with the apparent crystal morphology. Another imine-linked COF film [TPB-dimethoxyterephthaldehyde (DMTP)-COF] was directly produced on the electrodes under mild conditions

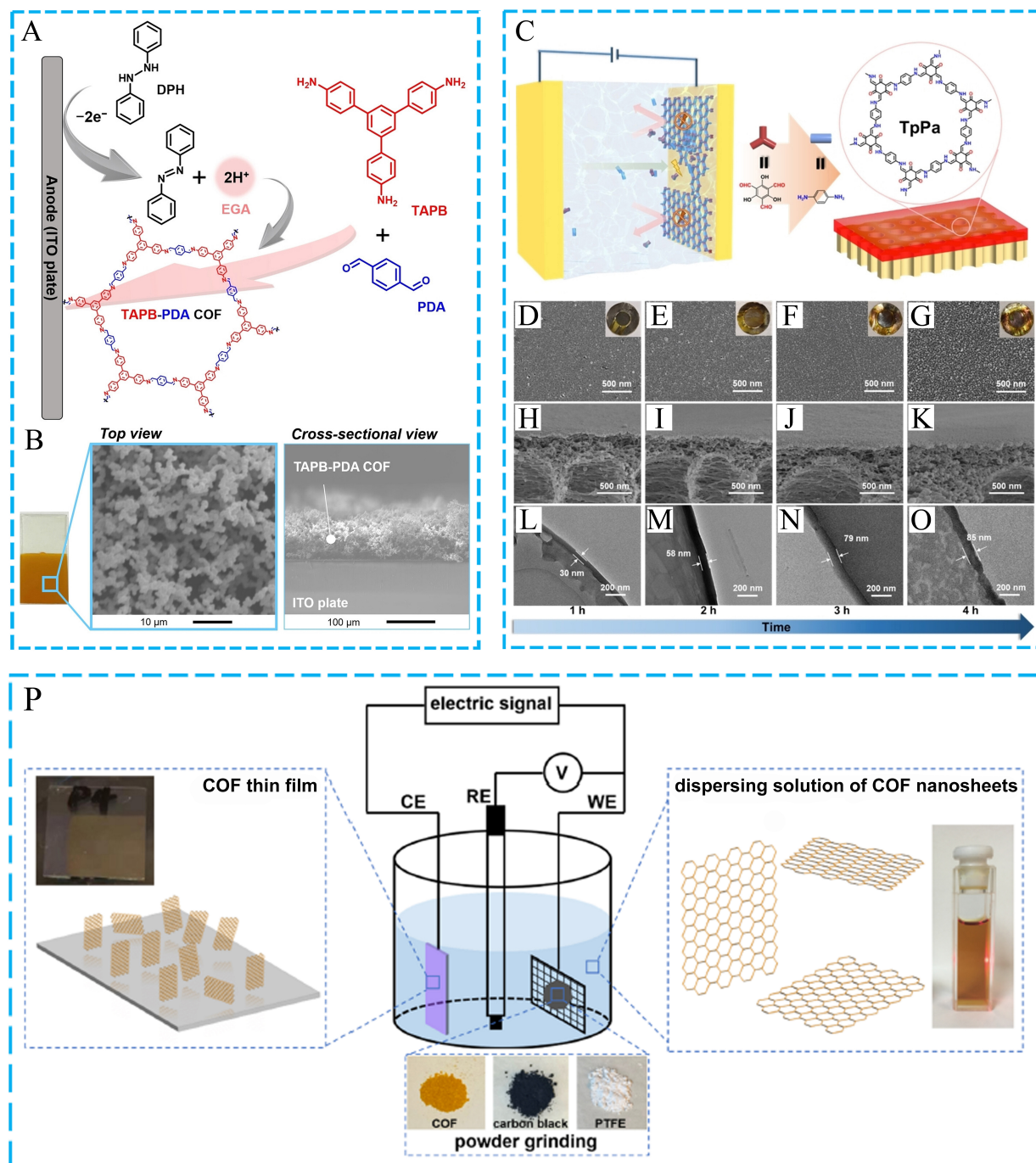


Figure 15. (A) The synthetic process of COFs on the electrode surface using EGA; (B) SEM image of the as-synthesized COF film; (C) The growth TpPa COF membrane on PAN via electrochemical polymerization; (D-K) SEM and (L-O) TEM images of TpPa membranes at different electropolymerization times; (P) Schematic representation for the electrochemical synthesis of COF membranes. (A and B) Adapted with permission^[139]. Copyright 2023, John Wiley and Sons. (C-O) Adapted with permission^[140]. Copyright 2023, John Wiley and Sons. (P) Adapted with permission^[141]. Copyright 2022, American Chemical Society. COFs: Covalent organic frameworks; EGA: electrogenerated acid; DPH: 1,2-diphenylhydrazine; TAPB: 1,3,5-tris(4-aminophenyl) benzene; PDA: terephthalaldehyde; SEM: scanning electron microscopy; Tp: 1,3,5-triformylphloroglucinol; Pa: p-phenylenediamine; PAN: polyacrylonitrile; TEM: transmission electron microscopy.

via an electrocleavage synthesis strategy [Figure 15P]^[141]. The COF powders were exfoliated to two-dimensional NSs at the cathode by the synergistic effect of electrochemical reduction and protonation. Subsequently, these COF NSs could migrate to the anode, resulting in the structural reconfiguration of COFs through the anodic oxidation. The COF membrane exhibited excellent crystallinity and hierarchical pores, which could be considered as an outstanding platform to accelerate the mass transfer process for realizing rapid and high iodine adsorption performance.

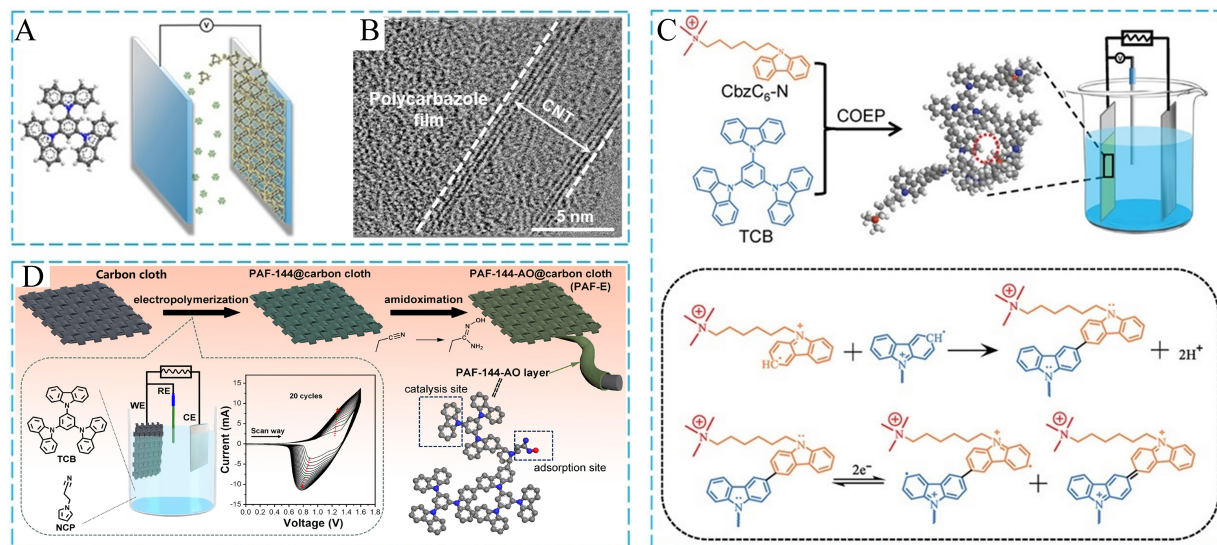


Figure 16. (A) The electropolymerization approach of TCB; (B) The TEM image of as-synthesized polycarbazoles on CNTs; (C) Schematic illustration of the fabrication and possible mechanism of the flexible ionic CMP membrane; (D) The fabrication diagram of self-standing PAFs. (A and B) Adapted with permission^[145]. Copyright 2021, American Chemical Society. (C) Adapted with permission^[146]. Copyright 2022, John Wiley and Sons. (D) Adapted with permission^[147]. Copyright 2023, American Chemical Society. TCB: 1,3,5-tris(*N*-carbazolyl)benzene; TEM: transmission electron microscopy; CNTs: carbon nanotubes; CMP: conjugated microporous polymer; COEP: coelectropolymerization; CbzC₆-N: 6-(9*H*-carbazol-9-yl)-*N,N,N*-trimethylhexan-1-aminium bromide; PAFs: porous aromatic frameworks; NCP: *N*-(2-cyanoethyl)-pyrrole.

Carbazole-based POFs are a major type of amorphous porous materials. The electroactive carbazole moiety can be utilized as a functional molecule to facilitate the electropolymerization coupling reaction^[142–144]. Recently, Zhou *et al.* designed and synthesized different polycarbazole-type CMPs using a scale-up electrochemical approach. One CMP was successfully prepared by the electropolymerization of 1,3,5-tris(*N*-carbazolyl)benzene (TCB) monomers [Figure 16A]^[145]. The thickness of CMP membranes could be controlled via the cyclic voltammetry (CV) scanning from -0.8 to 1.23 V. The TEM image of the as-synthesized composite showed that CMP was tightly connected to the carbon nanotube (CNT) substrate [Figure 16B]. Notably, CMP membranes have many advantages, including outstanding stability, large surface area, abundant pores, and uniform pore size, but their brittleness leads to extremely poor mechanical behavior. Hence, this research group further synthesized a flexible ionic CMP membrane with the precisely tailored pore architecture by a coelectropolymerization (COEP) strategy^[146]. As shown in Figure 16C, the CMP structure was constructed by two compositions, including the rigid TCB monomer for the uniform porous structure and the flexible charged CbzC₆-N monomer for the mechanical flexibility. Various functional sites were introduced into the organic building blocks via the rational monomer design, which could simultaneously introduce multifunctional sites into porous organic materials to achieve excellent performance. Moreover, electrochemical uranium extraction from seawater by PAFs also provided a new opportunity for the sustainable supply of nuclear fuel. In 2023, Chen *et al.* reported a facile electropolymerization and the following functionalization to grow PAF-144-AO (amidoxime group modified PAFs) with TCB and *N*-(2-cyanoethyl)-pyrrole (NCP) on carbon cloths. The self-standing and binder-free electrodes were successfully prepared for electrochemical uranium extraction [Figure 16D]^[147]. According to a series of comparative experiments, the amidoxime group, electroactive site, and porous framework synergistically improved uranium extraction performance via the adsorption-electro catalysis. This electrochemical process showed higher uptake and faster kinetics compared to the physicochemical adsorption.

The morphology and size of POFs can be precisely controlled by changing monomer concentration, potential, sweep speed, and other parameters in electrochemical synthesis. However, compared to other

green synthesis methods, there is relatively little research on the electrochemical synthesis strategy for synthesizing porous organic materials. The electrochemical synthesis strategy for POFs is still in the preliminary research stage. There are still many issues that require extensive research to determine, such as electroactive organic monomer, appropriate electrolyte, electropolymerization condition, and so on. In addition to the advantages of the electrochemical synthesis for preparing thin films, further exploration is needed on how to prepare high crystalline porous organic materials in large quantities.

Other green synthetic methods

Porous organic materials often need to be supplied with energy during the synthesis process. In addition to the above-mentioned green synthesis methods, some other environmentally friendly synthesis strategies with specific energy sources are summarized. In the field of green chemistry, some researchers have utilized diversified energy supply methods to controllably prepare porous organic materials, including microwave-assisted heating and photo-induced catalysis^[148,149].

For the microwave-assisted heating method, microwave radiation can produce a better temperature distribution in the synthetic system to eliminate the characteristic temperature distribution from the outside to the inside produced by the conventional heating method. Hence, the microwave-assisted green synthesis provides a favorable platform to prepare COFs with homogeneous morphology. For example, three two-dimensional imine-conjugated COFs with different functional group modifications were successfully synthesized using a simple microwave-assisted method for 1 h by Alsudairy *et al.* in 2023 [Figure 17A]^[150]. Compared with those samples obtained by the solvothermal method, the microwave-assisted COFs showed more homogeneous morphology, higher crystallinity, and larger yield. Due to the homogeneous spherical morphology and the high chemical stability caused by the built-in electron-donating groups, the as-synthesized material was used as an iodine adsorbent with the advantages of fast kinetics, high capacity, and excellent reusability. In the same year, another important work was reported by Wang *et al.* [Figure 17B]^[151]. A three-dimensional anionic COF [cyclodextrin (CD)-COF-Li] was synthesized by co-condensing both γ -CD and B(OMe)₃ in the presence of LiOH under microwave-assisted solvothermal conditions with high yield, energy efficiency, and good crystallinity. The as-synthesized COFs possessed good ion channels and oriented Li⁺ conduction paths, leading to their great potential application in the solid-state lithium-oxygen battery.

The photocatalytic synthesis has attracted widespread attention due to its energy-saving, high efficiency, economic, and environmentally friendly features. In 2022, Wu *et al.* reported a photocatalytic method for the synthesis of COFs [Figure 17C]^[152]. Under room temperature conditions, a photocatalytic synthesis of COFs was achieved by a reaction of 2,5-diamino-1,4-benzenediol dihydrochloride (DABD) and tetrabutylammonium salt of Eosin Y (TBA-eosin Y) assisted by 1,3,5-tris(4-formylphenyl)triazine (TFPT). The as-synthesized benzoxazole-linked COF LZU-191 possessed good stability and high crystallinity. The reaction mechanism of this strategy is photocatalytic cyclization under sunlight, oxygen, TBA-eosin Y, and *N*-methyl-2-pyrrolidone (NMP) [Figure 17D]. In addition, the preparation of porous polymer microspheres by photopolymerization is an attractive method due to the ability of ultraviolet (UV) light to initiate free radical polymerization^[153,154]. As seen in Figure 17E, the authors proposed an efficient, versatile, and tunable strategy for the preparation of porous polymer microspheres based on the UV photopolymerization^[155]. The authors utilized poly(vinyl alcohol) (PVA) solution as the aqueous phase. The photopolymerization materials and photoinitiators in an organic solution were used as the oil phase, which was rapidly mixed and photopolymerized with UV-induced photopolymerization to obtain the polymers after removing the PVA template. During this synthetic process, the organic solvent was encapsulated in the prepared microspheres to act as a co-solvent and pore-forming agent, which could be removed ultimately to leave pores in the microspheres. This method is important for green synthesis of porous organic polymers in only a few minutes at room temperature.

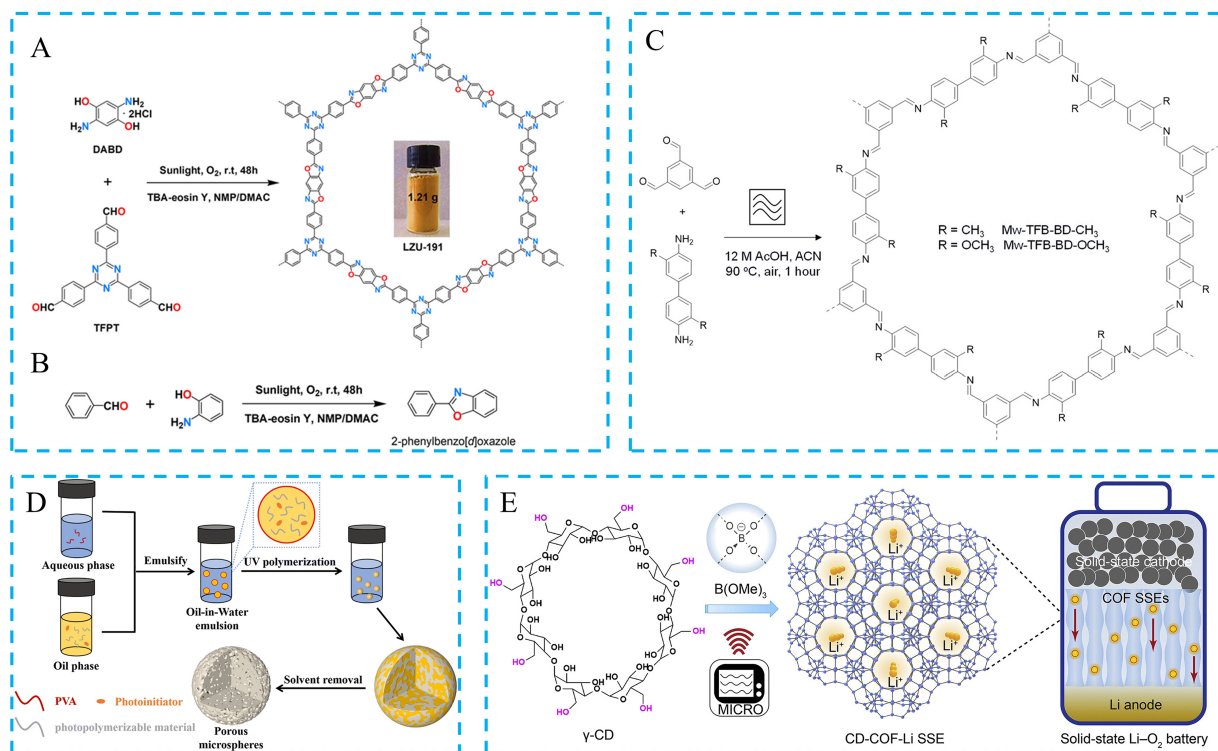


Figure 17. (A) The photopolymerization approach of Mw-TFB-BD-X COFs; (B) The synthesis diagram of CD-COF-Li for the solid-state Li-O₂ battery; (C) The preparation procedure of LZU-191 and (D) its model reaction for synthesizing 2-phenylbenzo[d]oxazole; (E) Schematic diagram of the preparation process of polymeric porous microspheres. (A) Adapted with permission^[150]. Copyright 2023, American Chemical Society. (B) Adapted with permission^[151]. Copyright 2022, Elsevier. (C and D) Adapted with permission^[152]. Copyright 2022, American Chemical Society. (E) Adapted with permission^[155]. Copyright 2023, Royal Society of Chemistry. COFs: Covalent organic frameworks; DABD: 2,5-diamino-1,4-benzenediol dihydrochloride; TBA-eosin Y: tetrabutylammonium salt of Eosin Y; NMP: N-methyl-2-pyrrolidone; TFPT: 1,3,5-tris(4-formylphenyl)triazine; UV: ultraviolet; PVA: poly(vinyl alcohol); SSE: solid-state electrolyte.

Overall, these synthesis strategies can shorten reaction time, simplify experimental manipulation, and substantially lower energy consumption. Additionally, they enable the design and synthesis of new POFs or different morphologies that are difficult to achieve through the conventional solvothermal method. This provides new ideas for expanding the synthesis strategy of POFs.

CONCLUSION AND OUTLOOK

Porous organic materials exhibit excellent performance in enormous applications, leading to their huge potential in industrial use. Compared to other industrially applied porous materials, such as zeolite and activated carbon, the synthesis process of most POFs does not satisfy the industrial needs, including low-energy consumption, non-pollution, good repeatability, easy operation, and large-scale preparation. As described in this review, an increasing number of POFs have been prepared by various environmentally friendly green synthesis strategies in recent years. However, many problems need to be solved to meet practical industrial applications. Herein, we highlight the challenge and direction for the green synthesis of POFs in the near future.

(1) The current research mainly focuses on the synthetic strategy and design principle for synthesizing POFs, but it clearly lacks the exploration on intermediate transition states, as well as in-depth analysis of synthesis mechanisms and reaction pathways. Amorphous porous organic materials, including PAFs, CMPs and HCPs, have been synthesized mainly through Friedel-Crafts alkylation, Suzuki coupling, Yamamoto coupling, and Sonogashira-Hagihara cross-coupling reactions with clear catalytic mechanisms. However, the effects of new reaction media or reaction methods on the formation, growth and crystallization of COFs are

not fully understood. The mechanism study is crucial for optimizing synthesis conditions, which plays a guiding role in the green synthetic process of POFs. The theoretical calculation is a useful method to investigate the possible reaction path. Meanwhile, the largest energy barrier between different intermediates can be determined as the rate-determining step by the calculated energy barrier, which is beneficial for preliminary determination of suitable reaction conditions, such as temperature, catalyst, potential, and so on. Furthermore, varieties of *in-situ* characterization techniques, including Fourier transform infrared spectra, Raman spectra and electron spin resonance spectroscopy, can be performed to verify intermediate products from an experimental perspective. On the other hand, time-resolved nuclear magnetic resonance, X-ray diffraction, and mass spectroscopy techniques can be further utilized to study the change of crystal phase, organic linker exchange, polymerization reaction, self-assembly, *etc.* Based on the above theoretical and experimental analysis, it is possible to preliminarily explore different green synthesis process conditions, monomers and polymerization reactions.

(2) For most organic coupling reactions in the POF synthesis, different types of catalysts are often required to promote the reaction occurrence. Catalysts can significantly reduce the reaction energy barrier, which is beneficial for achieving the efficient synthesis of POFs under green and mild conditions. However, most catalysts are not only expensive, but also difficult to separate and contaminate the targeted POFs. Especially, some catalysts are always sensitive to both air and water, leading to the harsh reaction conditions with a significant impact on the structure and crystallinity of POFs in the large-scale synthesis. Therefore, the development of high-performance and low-cost catalysts is crucial for the green synthesis of porous organic materials. The ideal catalyst should have the following characteristics: low cost, high catalytic activity, easy separation, good stability, and available reproducibility even in the large-scale preparation. In addition to the above characteristics, the low life-cycle cost, high security, fine reusability and sustainability of catalysts should be comprehensively evaluated and considered in the catalyst-assisted green and industrial synthesis system.

(3) It is urgently in need of extensive research on more efficient, green, scalable, and sustainable synthesis methods, leading to the transformation from the laboratory synthesis to the industrial large-scale preparation of POFs. Some synthetic technologies, such as extrusion or spray drying, may enhance the productivity of the large-scale synthesis, even exceeding the laboratory scale. Therefore, considering the practical requirements such as industrial equipment, energy conservation, environmental protection, product quality, separation and purification, the suitable green scale synthesis processes of the targeted POFs should be developed and investigated in detail.

In summary, porous organic materials exhibit great potential in various applications. POFs have attracted much attention and research, hoping to realize practical applications and breakthroughs in industrial fields. In fact, many aspects limit the industrial practical application of POFs from the laboratory level. One of the key factors is the development of green scale synthesis processes. Up to now, various green synthetic strategies, including room temperature, green solvent, solvent-free, mechanochemical and electrochemical synthesis, have been developed to prepare different POFs. Nevertheless, the current research on green synthesis processes is slightly immature and there is still a significant gap from the practical application. Further development in this field needs collaboration from multiple multidisciplinary experts. We believe that scientific researchers will achieve more excellent results and push the industrial application of POFs to a new level in the future.

DECLARATIONS

Authors' contributions

Investigation, methodology, data curation, writing original draft: Wen, H. M.

Writing original draft: Zhang, S.

Methodology, conceptualization, formal analysis: Li, P.

Formal analysis: Kong, X.

Writing - review and editing: Yuan, R.

Supervision, writing - review and editing: He, H.

Availability of data and materials

Not applicable.

Financial support and sponsorship

None.

Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Copyright

© The Author(s) 2026.

REFERENCES

1. Zhao, D.; Zhao, T. Pore engineering for high performance porous materials. *ACS. Cent. Sci.* **2023**, *9*, 1499-503. DOI PubMed PMC
2. Wang, Y.; Tong, C.; Liu, Q.; Han, R.; Liu, C. Intergrowth zeolites, synthesis, characterization, and catalysis. *Chem. Rev.* **2023**, *123*, 11664-721. DOI PubMed
3. Chen, L. H.; Sun, M. H.; Wang, Z.; Yang, W.; Xie, Z.; Su, B. L. Hierarchically structured zeolites: from design to application. *Chem. Rev.* **2020**, *120*, 11194-294. DOI PubMed
4. Yang, C.; Zhao, T.; Pan, H.; Liu, F.; Cao, J.; Lin, Q. Facile preparation of N-doped porous carbon from chitosan and NaNH₂ for CO₂ adsorption and conversion. *Chem. Eng. J.* **2022**, *432*, 134347. DOI
5. Oliveira, A. D. N. D.; Cardoso, R. D. S.; Ferreira, I. M.; et al. Valorization of silica-based residues for the synthesis of ordered mesoporous silicas and their applications. *Micropor. Mesopor. Mat.* **2023**, *354*, 112520. DOI
6. Su, Z.; Chen, T. Porous noble metal electrocatalysts: synthesis, performance, and development. *Small* **2021**, *17*, e2005354. DOI PubMed
7. Hajivand, P.; Carolus, Jansen, J.; Pardo, E.; Armentano, D.; Mastropietro, T. F.; Azadmehr, A. Application of metal-organic frameworks for sensing of VOCs and other volatile biomarkers. *Coordin. Chem. Rev.* **2024**, *501*, 215558. DOI
8. Tian, Y.; Deng, C.; Peng, Y.; Zhang, X.; Zhang, Z.; Zaworotko, M. J. State of the art, challenges and prospects in metal-organic frameworks for the separation of binary propylene/propane mixtures. *Coordin. Chem. Rev.* **2024**, *506*, 215697. DOI
9. Hao, Q.; Tao, Y.; Ding, X.; et al. Porous organic polymers: a progress report in China. *Sci. China. Chem.* **2023**, *66*, 620-82. DOI
10. Diercks, C. S.; Yaghi, O. M. The atom, the molecule, and the covalent organic framework. *Science* **2017**, *355*, eaal1585. DOI PubMed
11. Liu, M.; Huang, Q.; Wang, S.; et al. Crystalline covalent triazine frameworks by in situ oxidation of alcohols to aldehyde monomers. *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 11968-72. DOI PubMed
12. Yuan, Y.; Yang, Y.; Zhu, G. Molecularly imprinted porous aromatic frameworks for molecular recognition. *ACS. Cent. Sci.* **2020**, *6*, 1082-94. DOI PubMed PMC
13. Ma, Y.; Cui, F.; Rong, H.; et al. Continuous porous aromatic framework membranes with modifiable sites for optimized gas separation. *Angew. Chem. Int. Ed. Engl.* **2022**, *61*, e202113682. DOI PubMed
14. Shen, X.; Faheem, M.; Matsuo, Y.; et al. Polarity engineering of porous aromatic frameworks for specific water contaminant capture. *J. Mater. Chem. A* **2019**, *7*, 2507-12. DOI
15. Gong, J.; Lin, R.; Chen, B. Conjugated microporous polymers with rigid backbones for organic solvent nanofiltration. *Chem* **2018**, *4*, 2269-71. DOI
16. Tantisriyanurak, S.; Duguid, H. N.; Peattie, L.; Dawson, R. Acid functionalized conjugated microporous polymers as a reusable catalyst for biodiesel production. *ACS. Appl. Polym. Mater.* **2020**, *2*, 3908-15. DOI
17. Giri, A.; Biswas, S.; Hussain, M. W.; Dutta, T. K.; Patra, A. Nanostructured hypercrosslinked porous organic polymers: morphological evolution and rapid separation of polar organic micropollutants. *ACS. Appl. Mater. Interfaces* **2022**, *14*, 7369-81. DOI PubMed

18. Zhang, W.; Ma, F.; Ma, L.; Zhou, Y.; Wang, J. Imidazolium-functionalized ionic hypercrosslinked porous polymers for efficient synthesis of cyclic carbonates from simulated flue gas. *ChemSusChem* **2020**, *13*, 341–50. [DOI PubMed](#)
19. Ren, H.; Zhu, G. Porous organic frameworks: synthetic strategy and their applications. *Acta. Chim. Sinica*. **2015**, *73*, 587. [DOI](#)
20. Li, W.; Xiao, W.; Luo, Q.; et al. Ionic liquids promoted synthesis, enhanced functions, and expanded applications of porous organic frameworks. *Coordin. Chem. Rev.* **2023**, *493*, 215304. [DOI](#)
21. He, C.; Wang, Y.; Chen, Y.; et al. Microregulation of pore channels in covalent-organic frameworks used for the selective and efficient separation of ethane. *ACS. Appl. Mater. Interfaces*. **2020**, *12*, 52819–25. [DOI PubMed](#)
22. Liu, Y.; Wang, S.; Meng, X.; et al. Molecular expansion for constructing porous organic polymers with high surface areas and well-defined nanopores. *Angew. Chem. Int. Ed. Engl.* **2020**, *59*, 19487–93. [DOI PubMed](#)
23. Cao, L.; Wang, C.; Wang, H.; et al. Rationally designed cyclooctatetrathiophene-based porous aromatic frameworks (COT-PAFs) for efficient photocatalytic hydrogen peroxide production. *Angew. Chem. Int. Ed. Engl.* **2024**, *63*, e202402095. [DOI PubMed](#)
24. Hauser, B. G.; Farha, O. K.; Exley, J.; Hupp, J. T. Thermally enhancing the surface areas of Yamamoto-derived porous organic polymers. *Chem. Mater.* **2013**, *25*, 12–6. [DOI](#)
25. Zhang, Y.; Li, Z.; Zhang, C.; et al. Multifunctional porous organic polymers as ideal platforms for gas uptake, metal-ions sensing, and cell imaging. *Polym. Chem.* **2023**, *14*, 4199–204. [DOI](#)
26. Xue, Y.; Zhang, H.; Han, Z.; He, H. Electrochemical impedimetric aptasensors based on hyper-cross-linked porous organic frameworks for the determination of kanamycin. *J. Mater. Chem. C*. **2021**, *9*, 12566–72. [DOI](#)
27. He, H.; Wen, H.; Li, P.; et al. Tailor-made yolk-shell nanocomposites of star-shape Au and porous organic polymer for nitrogen electroreduction to ammonia. *Chem. Eng. J.* **2023**, *476*, 146760. [DOI](#)
28. Xu, Z.; Liu, K.; Wang, S.; et al. Viologen-based cationic radical porous organic polymers for visible-light-driven photocatalytic oxidation. *ACS. Appl. Polym. Mater.* **2024**, *6*, 701–11. [DOI](#)
29. Huang, J.; Peng, Q.; Liu, C.; et al. Microporous nitrogen-rich polymers via ullmann coupling reaction for selective adsorption of C₂H₂ over CH₄. *Chin. J. Chem.* **2023**, *41*, 514–20. [DOI](#)
30. Jadhav, T.; Fang, Y.; Patterson, W.; Liu, C. H.; Hamzehpoor, E.; Perepichka, D. F. 2D poly(arylene vinylene) covalent organic frameworks via aldol condensation of trimethyltriazine. *Angew. Chem. Int. Ed. Engl.* **2019**, *58*, 13753–7. [DOI PubMed](#)
31. Chen, Y.; Li, W.; Wang, X.; Gao, R.; Tang, A.; Kong, D. Green synthesis of covalent organic frameworks based on reaction media. *Mater. Chem. Front.* **2021**, *5*, 1253–67. [DOI](#)
32. Azadi, E.; Dinari, M. Green and facile preparation of covalent organic frameworks based on reaction medium for advanced applications. *Chemistry* **2023**, *29*, e202301837. [DOI PubMed](#)
33. Das, S.; Heasman, P.; Ben, T.; Qiu, S. Porous organic materials: strategic design and structure-function correlation. *Chem. Rev.* **2017**, *117*, 1515–63. [DOI PubMed](#)
34. Abdelnaby, M. M.; Cordova, K. E.; Abdulazeez, I.; et al. Novel porous organic polymer for the concurrent and selective removal of hydrogen sulfide and carbon dioxide from natural gas streams. *ACS. Appl. Mater. Interfaces*. **2020**, *12*, 47984–92. [DOI PubMed](#)
35. Fan, H.; Peng, M.; Strauss, I.; Mundstock, A.; Meng, H.; Caro, J. High-flux vertically aligned 2D covalent organic framework membrane with enhanced hydrogen separation. *J. Am. Chem. Soc.* **2020**, *142*, 6872–7. [DOI PubMed](#)
36. Nailwal, Y.; Devi, M.; Pal, S. K. Luminescent conjugated microporous polymers for selective sensing and ultrafast detection of picric acid. *ACS. Appl. Polym. Mater.* **2022**, *4*, 2648–55. [DOI](#)
37. Afshari, M.; Dinari, M.; Farrokhpour, H.; Zamora, F. Imine-linked covalent organic framework with a naphthalene moiety as a sensitive phosphate ion sensing. *ACS. Appl. Mater. Interfaces*. **2022**, *14*, 22398–406. [DOI PubMed PMC](#)
38. Zhang, Y.; Guo, J.; VanNatta, P.; et al. Metal-free heterogeneous asymmetric hydrogenation of olefins promoted by chiral frustrated lewis pair framework. *J. Am. Chem. Soc.* **2024**, *146*, 979–87. [DOI PubMed](#)
39. Chen, M.; Xiong, J.; Shi, Q.; et al. How the π bridge in donor- π -acceptor type covalent triazine frameworks influenced their photocatalytic hydrogen evolution performance. *Chem. Eng. J.* **2023**, *475*, 146099. [DOI](#)
40. Yang, S.; Chen, Z.; Zou, L.; Cao, R. Construction of thiadiazole-linked covalent organic frameworks via facile linkage conversion with superior photocatalytic properties. *Adv. Sci.* **2023**, *10*, e2304697. [DOI PubMed PMC](#)
41. Gu, C.; Huang, N.; Chen, Y.; et al. Porous organic polymer films with tunable work functions and selective hole and electron flows for energy conversions. *Angew. Chem. Int. Ed. Engl.* **2016**, *55*, 3049–53. [DOI PubMed](#)
42. Liao, C.; Liu, S. Tuning the physicochemical properties of reticular covalent organic frameworks (COFs) for biomedical applications. *J. Mater. Chem. B*. **2021**, *9*, 6116–28. [DOI PubMed](#)
43. Prakash, K.; Mishra, B.; Díaz, D. D.; Nagaraja, C. M.; Pachfule, P. Strategic design of covalent organic frameworks (COFs) for photocatalytic hydrogen generation. *J. Mater. Chem. A*. **2023**, *11*, 14489–538. [DOI](#)
44. Cui, K.; Tang, X.; Xu, X.; Kou, M.; Lyu, P.; Xu, Y. Crystalline dual-porous covalent triazine frameworks as a new platform for efficient electrocatalysis. *Angew. Chem. Int. Ed. Engl.* **2024**, *63*, e202317664. [DOI PubMed](#)

-
45. Xiong, S.; Guo, J.; Lv, F.; et al. Solvothermal synthesis and supercapacitive properties of highly electrochemical stable covalent organic frameworks with triazine building block. *J. Appl. Polym. Sci.* **2023**, *140*, e54538. [DOI](#)
46. Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. Porous, crystalline, covalent organic frameworks. *Science* **2005**, *310*, 1166-70. [DOI PubMed](#)
47. Li, H.; Chavez, A. D.; Li, H.; Li, H.; Dichtel, W. R.; Bredas, J. L. Nucleation and growth of covalent organic frameworks from solution: the example of COF-5. *J. Am. Chem. Soc.* **2017**, *139*, 16310-8. [DOI PubMed](#)
48. Li, X.; Jin, X.; Ma, L.; et al. Construction of borate-ester-based COFs with high specific surface area for the detection of H₂O content in the food field. *Microchem. J.* **2024**, *199*, 109976. [DOI](#)
49. Chang, P. H.; Sil, M. C.; Reddy, K. S. K.; Lin, C. H.; Chen, C. M. Polyimide-based covalent organic framework as a photocurrent enhancer for efficient dye-sensitized solar cells. *ACS Appl. Mater. Interfaces.* **2022**, *14*, 25466-77. [DOI PubMed](#)
50. DeBlase, C. R.; Silberstein, K. E.; Truong, T. T.; Abruña, H. D.; Dichtel, W. R. β -Ketoenamine-linked covalent organic frameworks capable of pseudocapacitive energy storage. *J. Am. Chem. Soc.* **2013**, *135*, 16821-4. [DOI PubMed](#)
51. Yu, H.; Wang, D. Metal-free magnetism in chemically doped covalent organic frameworks. *J. Am. Chem. Soc.* **2020**, *142*, 11013-21. [DOI PubMed](#)
52. Yang, C.; Hu, H.; Qian, C.; Liao, Y. Hollow sp²-conjugated covalent organic framework encapsulating thiophene-based photosensitizer for enhanced visible-light-driven hydrogen evolution. *J. Mater. Chem. A.* **2023**, *11*, 25899-909. [DOI](#)
53. Yang, N.; Gu, Y.; Shan, Y.; et al. Dual rate-modulation approach for the preparation of crystalline covalent triazine frameworks displaying efficient sodium storage. *ACS. Macro. Lett.* **2022**, *11*, 60-5. [DOI PubMed](#)
54. Martín-Illán, J.Á.; Suárez, J. A.; Gómez-Herrero, J.; et al. Ultralarge free-standing imine-based covalent organic framework membranes fabricated via compression. *Adv. Sci.* **2022**, *9*, e2104643. [DOI PubMed PMC](#)
55. Yao, B. J.; Li, J. T.; Huang, N.; et al. Pd NP-loaded and covalently cross-linked COF membrane microreactor for aqueous CBs dechlorination at room temperature. *ACS Appl. Mater. Interfaces.* **2018**, *10*, 20448-57. [DOI PubMed](#)
56. Parvatkar, P. T.; Kandambeth, S.; Shaikh, A. C.; et al. A tailored COF for visible-light photosynthesis of 2,3-dihydrobenzofurans. *J. Am. Chem. Soc.* **2023**, *145*, 5074-82. [DOI PubMed PMC](#)
57. Campbell, A.; Alsudairy, Z.; Dun, C.; et al. Dioxin-linked covalent organic framework-supported palladium complex for rapid room-temperature Suzuki–Miyaura coupling reaction. *Crystals* **2023**, *13*, 1268. [DOI](#)
58. Luan, T. X.; Du, L.; Wang, J. R.; et al. Highly effective generation of singlet oxygen by an imidazole-linked robust photosensitizing covalent organic framework. *ACS. Nano.* **2022**, *16*, 21565-75. [DOI PubMed](#)
59. Seo, J. M.; Noh, H. J.; Jeon, J. P.; et al. Conductive and ultrastable covalent organic framework/carbon hybrid as an ideal electrocatalytic platform. *J. Am. Chem. Soc.* **2022**, *144*, 19973-80. [DOI PubMed](#)
60. Jaryal, R.; Khullar, S.; Kumar, R. Benzothiazole-derived covalent organic framework for multimedia iodine uptake. *J. Clust. Sci.* **2024**, *35*, 461-79. [DOI](#)
61. Yang, Z.; Chen, H.; Wang, S.; et al. Transformation strategy for highly crystalline covalent triazine frameworks: from staggered AB to eclipsed AA stacking. *J. Am. Chem. Soc.* **2020**, *142*, 6856-60. [DOI PubMed](#)
62. Guo, L.; Wang, X.; Zhan, Z.; et al. Crystallization of covalent triazine frameworks via a heterogeneous nucleation approach for efficient photocatalytic applications. *Chem. Mater.* **2021**, *33*, 1994-2003. [DOI](#)
63. Wang, H.; Shi, L.; Qu, Z.; et al. Increasing donor-acceptor interactions and particle dispersibility of covalent triazine frameworks for higher crystallinity and enhanced photocatalytic activity. *ACS Appl. Mater. Interfaces.* **2024**, *16*, 2296-308. [DOI PubMed](#)
64. Ma, T.; Kapustin, E. A.; Yin, S. X.; et al. Single-crystal x-ray diffraction structures of covalent organic frameworks. *Science* **2018**, *361*, 48-52. [DOI PubMed](#)
65. Xu, H. S.; Luo, Y.; Li, X.; et al. Single crystal of a one-dimensional metallo-covalent organic framework. *Nat. Commun.* **2020**, *11*, 1434. [DOI PubMed PMC](#)
66. Wang, X.; Enomoto, R.; Murakami, Y. Ionic additive strategy to control nucleation and generate larger single crystals of 3D covalent organic frameworks. *Chem. Commun.* **2021**, *57*, 6656-9. [DOI PubMed](#)
67. Natraj, A.; Ji, W.; Xin, J.; et al. Single-crystalline imine-linked two-dimensional covalent organic frameworks separate benzene and cyclohexane efficiently. *J. Am. Chem. Soc.* **2022**, *144*, 19813-24. [DOI PubMed](#)
68. Zhou, Z.; Xiong, X. H.; Zhang, L.; et al. Linker-guided growth of single-crystal covalent organic frameworks. *J. Am. Chem. Soc.* **2024**, *146*, 3449-57. [DOI PubMed](#)
69. Zhou, Z.; Zhang, L.; Yang, Y.; et al. Growth of single-crystal imine-linked covalent organic frameworks using amphiphilic amino-acid derivatives in water. *Nat. Chem.* **2023**, *15*, 841-7. [DOI PubMed](#)
70. Liu, T.; Liu, G. Porous organic materials offer vast future opportunities. *Nat. Commun.* **2020**, *11*, 4984. [DOI PubMed PMC](#)
71. Wang, W.; Zhou, M.; Yuan, D. Carbon dioxide capture in amorphous porous organic polymers. *J. Mater. Chem. A.* **2017**, *5*, 1334-47. [DOI](#)

-
72. Zhang, Y.; Riduan, S. N. Functional porous organic polymers for heterogeneous catalysis. *Chem. Soc. Rev.* **2012**, *41*, 2083–94. DOI PubMed
73. Ben, T.; Ren, H.; Ma, S.; et al. Targeted synthesis of a porous aromatic framework with high stability and exceptionally high surface area. *Angew. Chem. Int. Ed. Engl.* **2009**, *48*, 9457–60. DOI PubMed
74. Kim, J. H.; Kang, D. W.; Yun, H.; et al. Post-synthetic modifications in porous organic polymers for biomedical and related applications. *Chem. Soc. Rev.* **2022**, *51*, 43–56. DOI PubMed
75. Zhang, Z.; Liu, Z.; Xue, C.; Chen, H.; Han, X.; Ren, Y. Amorphous porous organic polymers containing main group elements. *Commun. Chem.* **2023**, *6*, 271. DOI PubMed PMC
76. Yuan, Y.; Meng, Q.; Faheem, M.; et al. A molecular coordination template strategy for designing selective porous aromatic framework materials for uranyl capture. *ACS. Cent. Sci.* **2019**, *5*, 1432–9. DOI PubMed PMC
77. Ma, T.; Zhao, R.; Li, Z.; et al. Efficient gold recovery from E-waste via a chelate-containing porous aromatic framework. *ACS. Appl. Mater. Interfaces.* **2020**, *12*, 30474–82. DOI PubMed
78. Li, B.; Sun, Q.; Zhang, Y.; et al. Functionalized porous aromatic framework for efficient uranium adsorption from aqueous solutions. *ACS. Appl. Mater. Interfaces.* **2017**, *9*, 12511–7. DOI PubMed
79. Luo, D.; Shi, T.; Li, Q. H.; et al. Green, general and low-cost synthesis of porous organic polymers in sub-kilogram scale for catalysis and CO₂ capture. *Angew. Chem. Int. Ed. Engl.* **2023**, *62*, e202305225. DOI PubMed
80. Park, J. I.; Jang, J. Y.; Ko, Y. J.; et al. Room-temperature synthesis of a hollow microporous organic polymer bearing activated alkyne IR probes for nonradical thiol-yne click-based post-functionalization. *Chem. Asian. J.* **2021**, *16*, 1398–402. DOI PubMed
81. Zhang, F.; Hong, M.; Liu, Z.; et al. Facile room-temperature synthesis of novel porous three-component hybrid covalent organic polymers and their applications towards sulfadiazine adsorption. *ChemistrySelect* **2019**, *4*, 12719–25. DOI
82. Zhao, Y.; Lu, W.; Zhang, Y.; Liu, X.; Sun, B. Room temperature synthesis of piperazine-based nitrogen-rich porous organic polymers for efficient iodine adsorption. *Micropor. Mesopor. Mat.* **2024**, *366*, 112954. DOI
83. Ma, W.; Zheng, Q.; He, Y.; et al. Size-controllable synthesis of uniform spherical covalent organic frameworks at room temperature for highly efficient and selective enrichment of hydrophobic peptides. *J. Am. Chem. Soc.* **2019**, *141*, 18271–7. DOI PubMed
84. Ma, W.; Li, G.; Zhong, C.; et al. Room-temperature controllable synthesis of hierarchically flower-like hollow covalent organic frameworks for brain natriuretic peptide enrichment. *Chem. Commun.* **2021**, *57*, 7362–5. DOI PubMed
85. Guo, L.; Zhang, Q. Y.; Yu, Z.; Krishna, R.; Luo, F. Minute and large-scale synthesis of covalent-organic frameworks in water at room temperature by a two-step dissolution–precipitation method. *Chem. Mater.* **2023**, *35*, 5648–56. DOI
86. Kong, X.; Wu, Z.; Strømme, M.; Xu, C. Ambient aqueous synthesis of imine-linked covalent organic frameworks (COFs) and fabrication of freestanding cellulose nanofiber@COF nanopapers. *J. Am. Chem. Soc.* **2024**, *146*, 742–51. DOI PubMed PMC
87. Liang, J.; Ruan, J.; Njagic, B.; et al. Insight into bioactivity of in-situ trapped enzyme-covalent-organic frameworks. *Angew. Chem. Int. Ed. Engl.* **2023**, *62*, e202303001. DOI PubMed
88. Zhou, D.; Tan, X.; Wu, H.; Tian, L.; Li, M. Synthesis of C–C bonded two-dimensional conjugated covalent organic framework films by Suzuki polymerization on a liquid-liquid interface. *Angew. Chem. Int. Ed. Engl.* **2019**, *58*, 1376–81. DOI PubMed
89. Sahabudeen, H.; Qi, H.; Ballabio, M.; et al. Highly crystalline and semiconducting imine-based two-dimensional polymers enabled by interfacial synthesis. *Angew. Chem. Int. Ed. Engl.* **2020**, *59*, 6028–36. DOI PubMed PMC
90. He, J.; Yu, L.; Li, Z.; Ba, S.; Lan, F.; Wu, Y. Catalyst regulated interfacial synthesis of self-standing covalent organic framework membranes at room temperature for molecular separation. *J. Colloid. Interface. Sci.* **2023**, *629*, 428–37. DOI PubMed
91. Wu, D.; Che, Q.; He, H.; et al. Room-temperature interfacial synthesis of vinylene-bridged two-dimensional covalent organic framework thin film for nonvolatile memory. *ACS. Mater. Lett.* **2023**, *5*, 874–83. DOI
92. Chen, J.; Li, R.; Liu, S.; et al. Surfactant-assisted interfacial polymerization towards high-crystallinity COF membranes for organic solvent nanofiltration. *J. Membrane. Sci.* **2024**, *694*, 122404. DOI
93. Li, K.; Zhu, J.; Liu, D.; Zhang, Y.; Van, der. Bruggen. B. Controllable and rapid synthesis of conjugated microporous polymer membranes via interfacial polymerization for ultrafast molecular separation. *Chem. Mater.* **2021**, *33*, 7047–56. DOI
94. Zhang, J.; Cheng, C.; Guan, L.; Jiang, H. L.; Jin, S. Rapid synthesis of covalent organic frameworks with a controlled morphology: an emulsion polymerization approach via the phase transfer catalysis mechanism. *J. Am. Chem. Soc.* **2023**, *145*, 21974–82. DOI PubMed
95. Shi, L.; Li, W.; Wu, Y.; et al. Controlled synthesis of mesoporous π -conjugated polymer nanoarchitectures as anodes for lithium-ion batteries. *Macromol. Rapid. Commun.* **2022**, *43*, e2100897. DOI PubMed
96. Zhao, W.; Yan, P.; Yang, H.; et al. Using sound to synthesize covalent organic frameworks in water. *Nat. Synth.* **2022**, *1*, 87–95. DOI
97. Wang, H.; Zhao, J.; Li, Y.; et al. Aqueous two-phase interfacial assembly of COF membranes for water desalination. *Nanomicro. Lett.* **2022**, *14*, 216. DOI PubMed PMC
98. Hu, F.; Hu, Z.; Liu, Y.; et al. Aqueous sol-gel synthesis and shaping of covalent organic frameworks. *J. Am. Chem. Soc.* **2023**, *145*, 27718–27. DOI PubMed

-
99. Zhang, Z.; Xu, Y. Hydrothermal synthesis of highly crystalline zwitterionic vinylene-linked covalent organic frameworks with exceptional photocatalytic properties. *J. Am. Chem. Soc.* **2023**, *145*, 25222–32. [DOI PubMed](#)
100. Yang, Y.; Sabaghi, D.; Liu, C.; et al. On-water surface synthesis of vinylene-linked cationic two-dimensional polymer films as the anion-selective electrode coating. *Angew. Chem. Int. Ed. Engl.* **2024**, *63*, e202316299. [DOI PubMed](#)
101. Liu, Y.; Wang, Y.; Li, H.; et al. Ambient aqueous-phase synthesis of covalent organic frameworks for degradation of organic pollutants. *Chem. Sci.* **2019**, *10*, 10815–20. [DOI PubMed PMC](#)
102. Martín-Illán, JÁ.; Rodríguez-San-Miguel, D.; Franco, C.; et al. Green synthesis of imine-based covalent organic frameworks in water. *Chem. Commun.* **2020**, *56*, 6704–7. [DOI PubMed](#)
103. Zhao, B.; He, M.; Chen, B.; Hu, B. Facile green synthesis of magnetic porous organic polymers for fast preconcentration of trace lead and mercury from environmental water followed by graphite furnace atomic absorption spectrometry detection. *Spectrochim. Acta. B.* **2022**, *196*, 106524. [DOI](#)
104. Huang, L.; He, M.; Chen, B.; Cheng, Q.; Hu, B. Facile green synthesis of magnetic porous organic polymers for rapid removal and separation of methylene blue. *ACS. Sustain. Chem. Eng.* **2017**, *5*, 4050–5. [DOI](#)
105. Kuhn, P.; Antonietti, M.; Thomas, A. Porous, covalent triazine-based frameworks prepared by ionothermal synthesis. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 3450–3. [DOI PubMed](#)
106. Dong, B.; Wang, D.; Wang, W.; Tian, X.; Ren, G. Post synthesis of a glycine-functionalized covalent triazine framework with excellent CO₂ capture performance. *Micropor. Mesopor. Mat.* **2020**, *306*, 110475. [DOI](#)
107. Jiang, K.; Peng, P.; Tranca, D.; et al. Covalent triazine frameworks and porous carbons: perspective from an azulene-based case. *Macromol. Rapid. Commun.* **2022**, *43*, e2200392. [DOI PubMed](#)
108. Mohamed, M. G.; Sharma, S. U.; Liu, N. Y.; et al. Ultrastable covalent triazine organic framework based on anthracene moiety as platform for high-performance carbon dioxide adsorption and supercapacitors. *Int. J. Mol. Sci.* **2022**, *23*, 3174. [DOI PubMed PMC](#)
109. Wang, G.; Leus, K.; Zhao, S.; Van, Der. Voort, P. Newly designed covalent triazine framework based on novel N-heteroaromatic building blocks for efficient CO₂ and H₂ capture and storage. *ACS. Appl. Mater. Interfaces.* **2018**, *10*, 1244–9. [DOI PubMed](#)
110. Mohamed, M. G.; El-mahdy, A. F. M.; Takashi, Y.; Kuo, S. Ultrastable conductive microporous covalent triazine frameworks based on pyrene moieties provide high-performance CO₂ uptake and supercapacitance. *New. J. Chem.* **2020**, *44*, 8241–53. [DOI](#)
111. Rangaraj, V. M.; Reddy, K. S. K.; Karanikolos, G. N. Ionothermal synthesis of phosphonitrilic-core covalent triazine frameworks for carbon dioxide capture. *Chem. Eng. J.* **2022**, *429*, 132160. [DOI](#)
112. Lan, Z. A.; Wu, M.; Fang, Z.; et al. Ionothermal synthesis of covalent triazine frameworks in a NaCl-KCl-ZnCl₂ eutectic salt for the hydrogen evolution reaction. *Angew. Chem. Int. Ed. Engl.* **2022**, *61*, e202201482. [DOI PubMed](#)
113. Wang, C.; Lyu, P.; Chen, Z.; Xu, Y. Green and scalable synthesis of atomic-thin crystalline two-dimensional triazine polymers with ultrahigh photocatalytic properties. *J. Am. Chem. Soc.* **2023**, *145*, 12745–54. [DOI PubMed](#)
114. Yu, S. Y.; Mahmood, J.; Noh, H. J.; et al. Direct synthesis of a covalent triazine-based framework from aromatic amides. *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 8438–42. [DOI PubMed](#)
115. Niu, F.; Shao, Z.; Tao, L.; Ding, Y. Covalent triazine-based frameworks for NH₃ gas sensing at room temperature. *Sensor. Actuat. B. Chem.* **2020**, *321*, 128513. [DOI](#)
116. Sun, T.; Liang, Y.; Luo, W.; Zhang, L.; Cao, X.; Xu, Y. A general strategy for kilogram-scale preparation of highly crystal-line covalent triazine frameworks. *Angew. Chem. Int. Ed. Engl.* **2022**, *61*, e202203327. [DOI PubMed](#)
117. Zhang, P.; Wang, Z.; Wang, S.; et al. Fabricating industry-compatible olefin-linked COF resins for oxoanion pollutant scavenging. *Angew. Chem. Int. Ed. Engl.* **2022**, *61*, e202213247. [DOI PubMed](#)
118. Wang, Z.; Zhang, Y.; Wang, T.; et al. Organic flux synthesis of covalent organic frameworks. *Chem* **2023**, *9*, 2178–93. [DOI](#)
119. Krusenbaum, A.; Grätz, S.; Tigineh, G. T.; Borchardt, L.; Kim, J. G. The mechanochemical synthesis of polymers. *Chem. Soc. Rev.* **2022**, *51*, 2873–905. [DOI PubMed PMC](#)
120. Kubota, K.; Ito, H. Mechanochemical cross-coupling reactions. *Trend. Chem.* **2020**, *2*, 1066–81. [DOI](#)
121. Leonardi, M.; Villacampa, M.; Menéndez, J. C. Multicomponent mechanochemical synthesis. *Chem. Sci.* **2018**, *9*, 2042–64. [DOI PubMed PMC](#)
122. Shinde, D. B.; Aiyappa, H. B.; Bhadra, M.; et al. A mechanochemically synthesized covalent organic framework as a proton-conducting solid electrolyte. *J. Mater. Chem. A.* **2016**, *4*, 2682–90. [DOI](#)
123. Liu, W.; Cao, Y.; Wang, W.; et al. Mechanochromic luminescent covalent organic frameworks for highly selective hydroxyl radical detection. *Chem. Commun.* **2018**, *55*, 167–70. [DOI PubMed](#)
124. Zhang, X.; Xue, S.; Yan, Y.; Liu, S.; Ye, Q.; Zhou, F. Mechanochemical synthesis of thiadiazole functionalized COF as oil-based lubricant additive for reducing friction and wear. *Langmuir* **2024**, *40*, 4373–81. [DOI PubMed](#)

-
125. Rajput, L.; Banerjee, R. Mechanochemical synthesis of amide functionalized porous organic polymers. *Cryst. Growth. Des.* **2014**, *14*, 2729–32. [DOI](#)
126. Li, G.; Ye, J.; Fang, Q.; Liu, F. Amide-based covalent organic frameworks materials for efficient and recyclable removal of heavy metal lead (II). *Chem. Eng. J.* **2019**, *370*, 822–30. [DOI](#)
127. Jie, K.; Zhou, Y.; Sun, Q.; et al. Mechanochemical synthesis of pillar[5]quinone derived multi-microporous organic polymers for radioactive organic iodide capture and storage. *Nat. Commun.* **2020**, *11*, 1086. [DOI](#) [PubMed](#) [PMC](#)
128. Troschke, E.; Grätz, S.; Lübken, T.; Borchardt, L. Mechanochemical Friedel-Crafts alkylation—A sustainable pathway towards porous organic polymers. *Angew. Chem. Int. Ed. Engl.* **2017**, *56*, 6859–63. [DOI](#) [PubMed](#)
129. Chen, X.; Yuan, Z.; Zhong, Y.; Sun, F.; Ren, H. Synthesis of a series of porous aromatic frameworks by mechanical ball milling. *New. J. Chem.* **2022**, *46*, 22504–8. [DOI](#)
130. Krusenbaum, A.; Geisler, J.; Kraus, F. J. L.; et al. The mechanochemical Friedel-Crafts polymerization as a solvent-free cross-linking approach toward microporous polymers. *J. Polym. Sci.* **2022**, *60*, 62–71. [DOI](#)
131. Yuan, R.; Yan, Z.; Shaga, A.; He, H. Solvent-free mechanochemical synthesis of a carbazole-based porous organic polymer with high CO₂ capture and separation. *J. Solid. State. Chem.* **2020**, *287*, 121327. [DOI](#)
132. Krusenbaum, A.; Kraus, F. J. L.; Hutsch, S.; et al. The rapid mechanochemical synthesis of microporous covalent triazine networks: elucidating the role of chlorinated linkers by a solvent-free approach. *Adv. Sustain. Syst.* **2023**, *7*, 2200477. [DOI](#)
133. Pan, Q.; Xu, Z.; Deng, S.; et al. A mechanochemically synthesized porous organic polymer derived CQD/chitosan-graphene composite film electrode for electrochemiluminescence determination of dopamine. *RSC. Adv.* **2019**, *9*, 39332–7. [DOI](#) [PubMed](#) [PMC](#)
134. Zhang, P.; Jiang, X.; Wan, S.; Dai, S. Charged porous polymers using a solid C–O cross-coupling reaction. *Chemistry* **2015**, *21*, 12866–70. [DOI](#) [PubMed](#)
135. Hou, S.; Meng, M.; Liu, D.; Zhang, P. Mechanochemical process to construct porous ionic polymers by menshutkin reaction. *ChemSusChem* **2021**, *14*, 3059–63. [DOI](#) [PubMed](#)
136. Tao, Y.; Liu, H.; Kong, H. Y.; et al. Electrochemical preparation of porous organic polymer films for high-performance memristors. *Angew. Chem. Int. Ed. Engl.* **2022**, *61*, e202205796. [DOI](#) [PubMed](#)
137. Zhang, M.; Jing, X.; Zhao, S.; et al. Electropolymerization of molecular-sieving polythiophene membranes for H₂ separation. *Angew. Chem. Int. Ed. Engl.* **2019**, *58*, 8768–72. [DOI](#) [PubMed](#)
138. Gu, C.; Huang, N.; Chen, Y.; et al. π -Conjugated microporous polymer films: designed synthesis, conducting properties, and photoenergy conversions. *Angew. Chem. Int. Ed. Engl.* **2015**, *54*, 13594–8. [DOI](#) [PubMed](#) [PMC](#)
139. Shirokura, T.; Hirohata, T.; Sato, K.; et al. Site-selective synthesis and concurrent immobilization of imine-based covalent organic frameworks on electrodes using an electrogenerated acid. *Angew. Chem. Int. Ed. Engl.* **2023**, *62*, e202307343. [DOI](#) [PubMed](#)
140. Wang, M.; Wang, Y.; Zhao, J.; et al. Electrochemical interfacial polymerization toward ultrathin COF membranes for brine desalination. *Angew. Chem. Int. Ed. Engl.* **2023**, *62*, e202219084. [DOI](#) [PubMed](#)
141. Wang, L.; Xu, C.; Zhang, W.; et al. Electrocleavage synthesis of solution-processed, imine-linked, and crystalline covalent organic framework thin films. *J. Am. Chem. Soc.* **2022**, *144*, 8961–8. [DOI](#) [PubMed](#)
142. Gu, C.; Huang, N.; Gao, J.; Xu, F.; Xu, Y.; Jiang, D. Controlled synthesis of conjugated microporous polymer films: versatile platforms for highly sensitive and label-free chemo- and biosensing. *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 4850–5. [DOI](#) [PubMed](#)
143. Long, J.; Liu, Y.; Huang, Z.; et al. Electropolymerization of preferred-oriented conjugated microporous polymer films for enhanced fluorescent sensing. *Chemistry* **2024**, *30*, e202304268. [DOI](#) [PubMed](#)
144. Gu, C.; Huang, N.; Wu, Y.; Xu, H.; Jiang, D. Design of highly photofunctional porous polymer films with controlled thickness and prominent microporosity. *Angew. Chem. Int. Ed. Engl.* **2015**, *54*, 11540–4. [DOI](#) [PubMed](#) [PMC](#)
145. Zhou, Z.; Guo, D.; Shinde, D. B.; et al. Precise sub-angstrom ion separation using conjugated microporous polymer membranes. *ACS. Nano.* **2021**, *15*, 11970–80. [DOI](#) [PubMed](#)
146. Zhou, Z.; Shinde, D. B.; Guo, D.; et al. Flexible ionic conjugated microporous polymer membranes for fast and selective ion transport. *Adv. Funct. Mater.* **2022**, *32*, 2108672. [DOI](#)
147. Chen, D.; Li, Y.; Zhao, X.; et al. Self-standing porous aromatic framework electrodes for efficient electrochemical uranium extraction. *ACS. Cent. Sci.* **2023**, *9*, 2326–32. [DOI](#) [PubMed](#) [PMC](#)
148. Kim, S.; Park, C.; Lee, M.; et al. Rapid photochemical synthesis of sea-urchin-shaped hierarchical porous COF-5 and its lithography-free patterned growth. *Adv. Funct. Mater.* **2017**, *27*, 1700925. [DOI](#)
149. Wei, H.; Chai, S.; Hu, N.; Yang, Z.; Wei, L.; Wang, L. The microwave-assisted solvothermal synthesis of a crystalline two-dimensional covalent organic framework with high CO₂ capacity. *Chem. Commun.* **2015**, *51*, 12178–81. [DOI](#) [PubMed](#)
150. Alsudairy, Z.; Brown, N.; Yang, C.; et al. Facile microwave-assisted synthesis of 2D imine-linked covalent organic frameworks for exceptional iodine capture. *Precis. Chem.* **2023**, *1*, 233–40. [DOI](#) [PubMed](#) [PMC](#)

-
151. Wang, X.; Chi, X.; Li, M.; Guan, D.; Miao, C.; Xu, J. An integrated solid-state lithium-oxygen battery with highly stable anionic covalent organic frameworks electrolyte. *Chem* **2023**, *9*, 394-410. [DOI](#)
152. Wu, C. J.; Li, X. Y.; Li, T. R.; et al. Natural sunlight photocatalytic synthesis of benzoxazole-bridged covalent organic framework for photocatalysis. *J. Am. Chem. Soc.* **2022**, *144*, 18750-5. [DOI PubMed](#)
153. Wang, F.; Qiu, Y.; Wang, B.; Wang, H.; Long, Y. Green method to fabricate porous microspheres for ultrasensitive SERS detection using UV light. *RSC. Adv.* **2016**, *6*, 100519-25. [DOI](#)
154. Jaszcz, K. Highly porous crosslinked poly(ester-anhydride) microspheres with high loading efficiency. *Chin. J. Polym. Sci.* **2015**, *33*, 1271-82. [DOI](#)
155. Tao, J.; Wu, K.; Chen, Y.; et al. A facile one-pot strategy for the preparation of porous polymeric microspheres via UV irradiation-induced polymerization in emulsions. *Soft. Matter.* **2023**, *19*, 1407-17. [DOI PubMed](#)

Disclaimer/Publisher's Note: All statements, opinions, and data contained in this publication are solely those of the individual author(s) and contributor(s) and do not necessarily reflect those of OAE and/or the editor(s). OAE and/or the editor(s) disclaim any responsibility for harm to persons or property resulting from the use of any ideas, methods, instructions, or products mentioned in the content.



© The Author(s) 2026. Open Access This article is licensed under a Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, sharing, adaptation, distribution and reproduction in any medium or format, for any purpose, even commercially, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.