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# Synthesis, Properties, and Their Potential Application of Covalent Organic Frameworks (COFs)

*Lifeng Deng, Junfeng Zhang and Yanan Gao*

## Abstract

Covalent organic frameworks (COFs) represent an emerging class of crystalline porous polymers, which are ingeniously assembled with organic building blocks through reversible covalent bonds. The well-defined crystalline porous structures, easy functional modification, high surface area, together with structural designability and diversity have offered the COFs superior potential in various applications, such as catalysis, gas adsorption and separation, and optoelectricity. Since the pioneer work of Omar Yaghi in 2005, this field has developed rapidly and attracted much attention from researchers with diverse expertise. In this chapter, we describe the basic design concepts, the recent synthetic advancements, and the frontiers of functional exploration in gas adsorption and storage. Special emphasis is placed on their potential application in heterogeneous catalysis field. Finally, the prospects of COFs and remaining issues in these fields are indicated.

**Keywords:** covalent organic framework, porous organic polymers, catalysis, gas adsorption, topological structure

## 1. Introduction

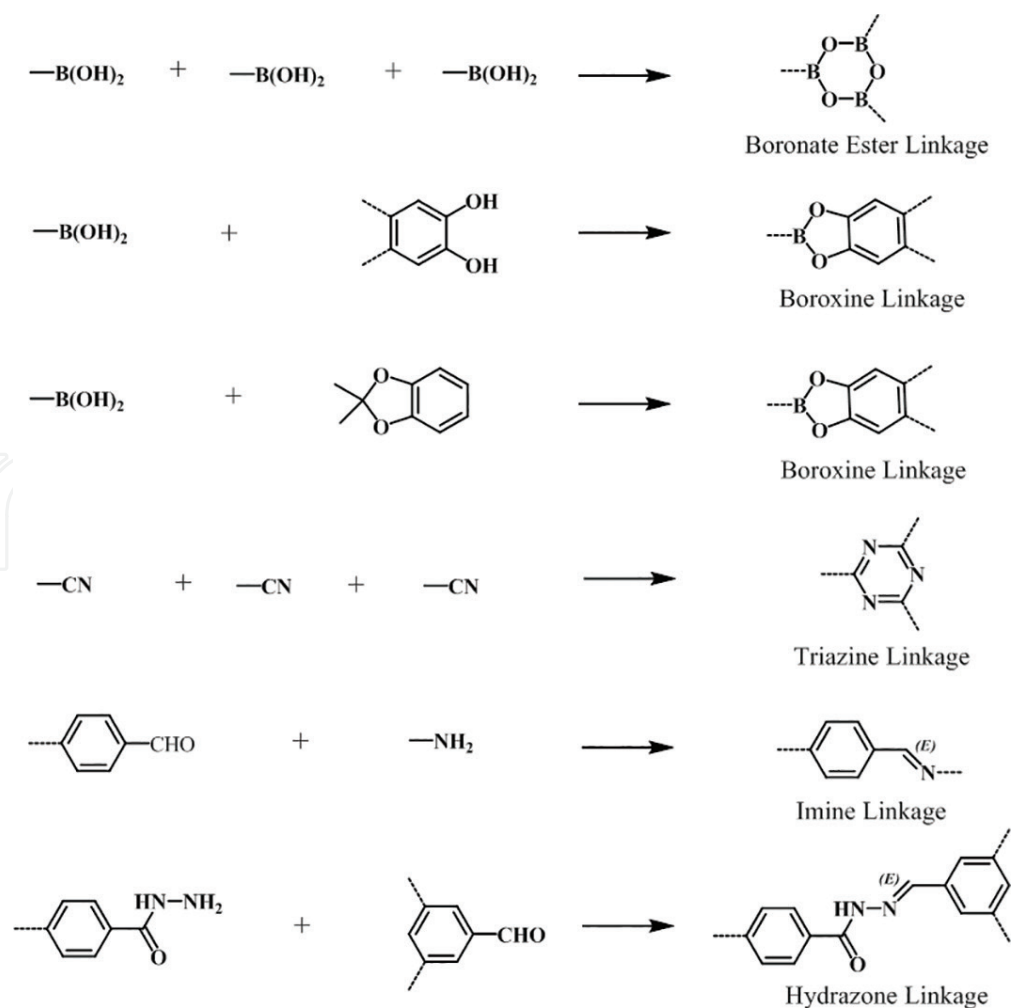
Over the years, interest in the field of porous materials has grown extremely due to their good performance and potential applications in gas storage and separation, catalysis, energy conversion and storage, and optoelectronics. Although a variety of porous materials have been synthesized by various ways, it has proven difficult to prepare organic polymer networks with discrete pores. However, the appearance of reticular chemistry makes it possible to construct these porous materials, which can be synthesized by using topologically designed building blocks.

The first family of such porous materials synthesized based on reticular chemistry is metal-organic frameworks (MOFs), which consist of metal ions or clusters coordinated to organic ligands to form one-, two-, or three-dimensional network structures [1]. The coordination versatility of the metal ions, combined with the functional diversity of the organic linkers gives these materials immense possibilities. Another family of porous materials to be synthesized on the base of reticular chemistry is covalent organic frameworks (COFs), which were firstly demonstrated by Yaghi and co-workers in 2005 [2]. Different from MOFs, COFs are constructed by pure organic building blocks to form crystalline porous polymers via reversible

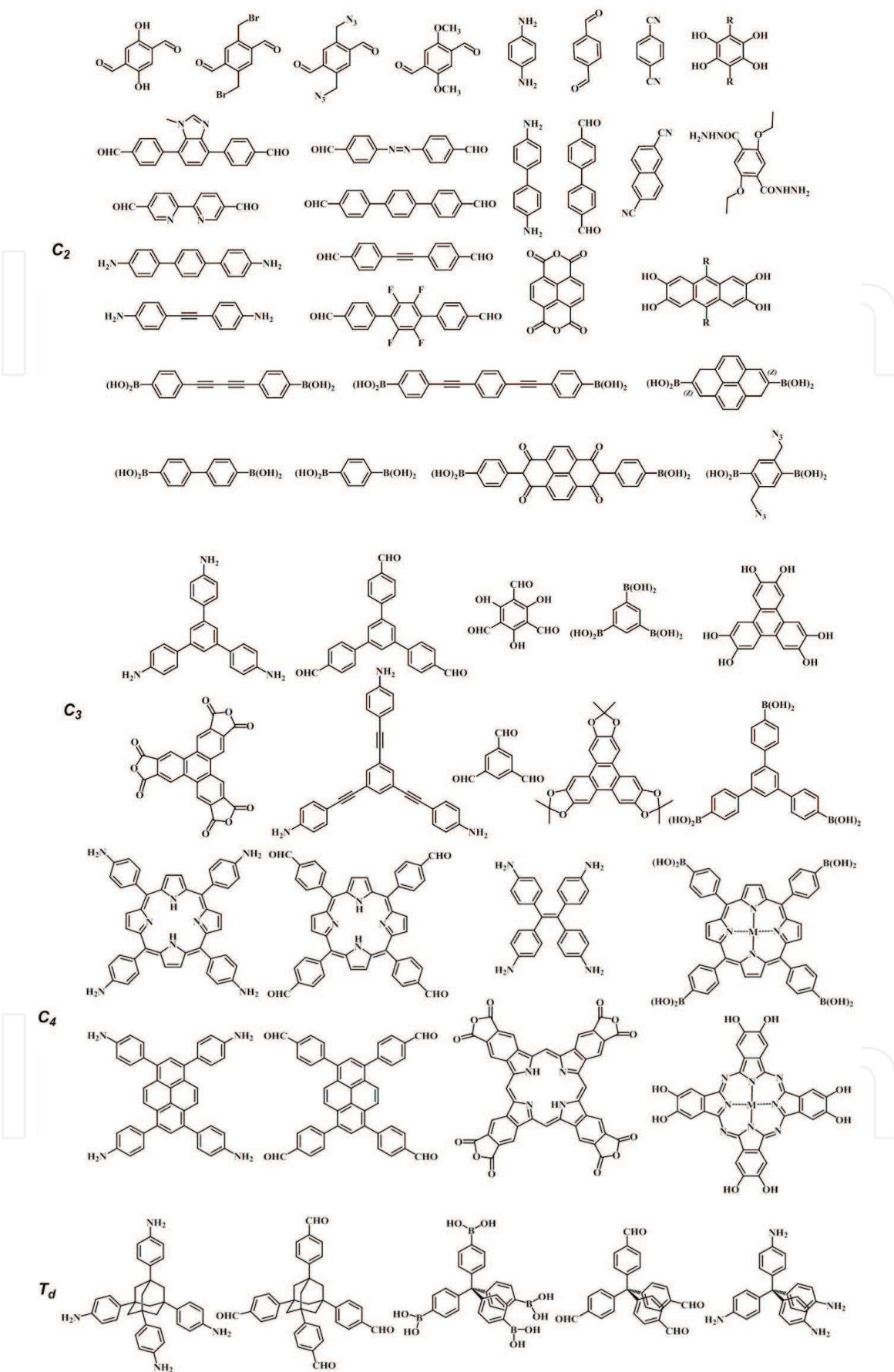
covalent bonds with predictable control over composition, topology, and porosity [3, 4]. Therefore, COFs could be regarded as “organic zeolites.”

In principle, the formation of COFs by linking organic building blocks is expected to be thermodynamically unfavorable. In many cases, amorphous cross-linked polymers or poorly defined solids are often obtained through the linkage of organic building blocks with strong covalent bonds. In order to obtain a crystalline material, the formation of linkages must be reversible and the reaction rates should be on a time scale that allows for defects to be self-corrected. Dynamic covalent chemistry (DCC) realizes the reversible formation of strong covalent bonds, which can be formed, broken, and reformed under certain conditions [5]. DCC is thermodynamically controlled and can endow reversible reaction systems with “error checking” and “proof-reading” features, which produces the most thermodynamically stable structures. Therefore, reversible covalent bond as linkages is considered to be prerequisite to construct crystalline COF materials. So far, the organic linkages involved in the formation of COFs include B-O (boroxine, boronate ester, spiroborate, and borosilicate), C=N (imine, hydrazone, and squaraine), C-N ( $\beta$ -ketoenamine, imide, and amide), etc. (**Figure 1**) [3].

In addition to reversible covalent bonds, the structure of the building blocks has to be considered to obtain crystalline COFs. During the formation process of COFs, the geometry of the building blocks needs to be well preserved in the COF framework. So, the desired building blocks should be structurally rigid, and the formation direction of reversible covalent bonds must be discrete [3]. From the



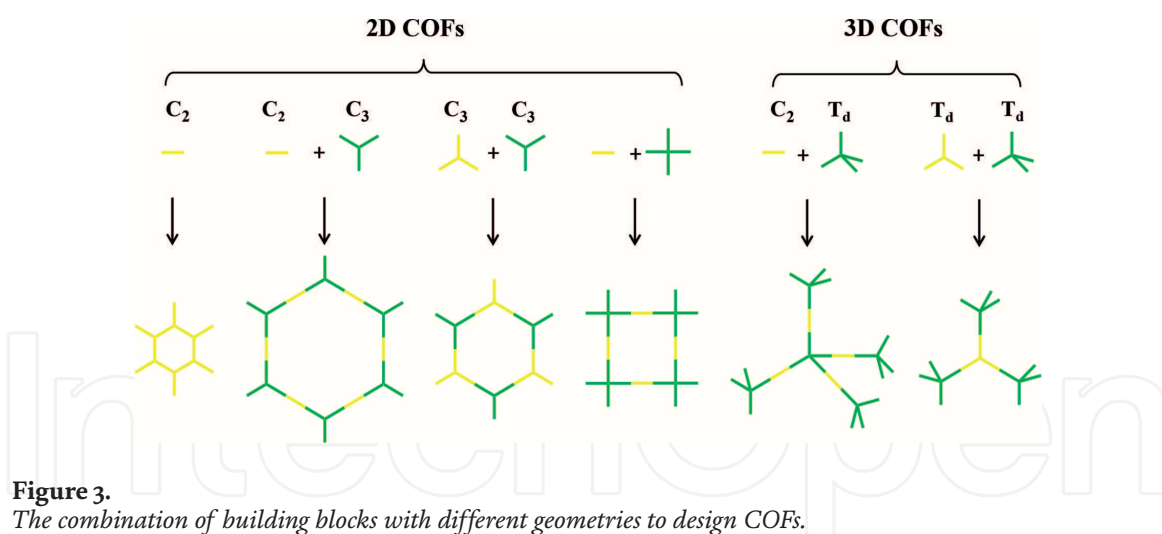
**Figure 1.** Schematic representation of the dynamic chemical reactions for the preparation of various COFs ([3]-Reproduced by permission of The Royal Society of Chemistry).



**Figure 2.**  
*The geometry of the building blocks for the preparation of COFs.*

viewpoint of geometric structure, these building blocks can be classified into 2D or 3D structure based on simplified symmetry notation, which refers to the directional symmetry of the reactive groups. The reported building blocks (2D- $C_2$ , 2D- $C_3$ ,





2D- $C_4$ , and 3D- $T_d$ ) are summarized in **Figure 2**. The COF structure is determined by the geometry of the building blocks. For example, the combinations of 2D building blocks, like 2D- $C_2$  + 2D- $C_3$ , 2D- $C_3$  + 2D- $C_3$ , or 2D- $C_2$  + 2D- $C_4$ , will lead to 2D COFs with predesigned topology and pore structure (**Figure 3**).

In contrast, the self-condensation of  $T_d$  building blocks (3D- $T_d$  + 3D- $T_d$ ) or the combinations of  $T_d$  building blocks with 2D building blocks such as 3D- $T_d$  + 2D- $C_2$ , 3D- $T_d$  + 2D- $C_3$ , or 3D- $T_d$  + 2D- $C_4$  allow for the construction of 3D COFs with different crystalline networks (**Figure 3**). Unlike the rapid expansion of 2D COFs, the progress in 3D COF chemistry has been severely impeded due to the limited choice of monomers. Therefore, only a few 3D COFs have been reported so far [6]. The rigid structure and discrete bonding direction of aromatics make them ideal building blocks for constructing COFs. The diversity of aromatic compounds allows a number of building block combinations, which makes it possible that the COFs have high flexibility in their molecular design.

## 2. Synthesis of COFs and their properties

Though many building units have been developed, it is still not an easy issue for constructing COFs with both high porosity and crystallinity. Because, it is also important to find suitable conditions under which reversible bond formation is possible without resorting to extreme temperatures or pressures. In other words, a synthetic method is another key to obtain crystalline COFs. A suitable temperature and pressure are required, and the appropriate solvent combinations and ratios are of specially importance in getting the balance between framework formation and crystallization [3]. In general, a high temperature (80–120°C) combined with a low reaction pressure is used to synthesize COFs. As for reaction medium, to date, almost all COFs, as either bulk materials or thin films grown on the support surface, have been obtained under solvothermal synthesis conditions. A traditional organic solvent or a solvent mixture has been used as a reaction medium. Besides, molten metal salts, including molten  $ZnCl_2$  and ionic liquids, have been attempted to provide ionothermal conditions for the synthesis of COFs. Regarding heating fashion to reaction system, microwave-assisted heating has proved to be quick to synthesize COFs under solvothermal conditions.

### 2.1 Solvothermal synthesis

As mentioned above, most of the reported COFs were obtained through the solvothermal synthesis method. The solvothermal synthesis of COFs often takes

3–7 days and requires heating at a high temperature within a sealed vessel. The pressure of the reaction system is of importance, which may affect the crystallinity and porosity of COFs significantly. In many cases, a 150 mTorr is the optimal pressure before the reaction system is sealed within a  $\sim 10\text{ cm}^3$  vessel. In addition, the solvent chosen for the formation of COFs is crucial as it governs the solubility of reactants and is closely related to reaction rate, crystal nucleation, crystal growth rate, and self-healing structure. Therefore, how to find an appropriate solvent system to get crystalline COFs has long been an intractable problem. A binary solvent mixture was generally used to obtain COFs in the presence of an acidic catalyst. For instance, solvent mixtures such as dioxane-mesitylene [2], DMAc-o-dichlorobenzene [7], and THF-methanol [8] have been employed to construct boronate ester-linked COFs. A mixture of dioxane-ethanol has been used as the solvent to synthesize imine-linked COFs [9], and even a ternary solvent system has been used to synthesize COF materials, in which a mixture of N-methyl-2-pyrrolidone (NMP), mesitylene, and isoquinoline afforded crystalline PI-COF-4 and PI-COF-5 with high yields after 5 days reaction [10]. In some cases, a single solvent has been found to be effective for getting crystalline COFs. For instance, a 3D COF, COF-DL229, has been recently synthesized by our group through the condensation reaction of tetrahedral 1,3,5,7-tetrakis(4-aminophenyl)-adamantane (TAPA) and linear 1,4-phthalaldehyde (PTA) in a sole solvent, 1,2-dichlorobenzene, and the resultant 3D COF exhibits high crystallinity and high BET surface area ( $1762\text{ m}^2\text{ g}^{-1}$ ) [11]. In addition, a suitable concentration of building blocks or the content of catalysis used in the solvent system is of significance for the reaction to proceed under thermodynamic control [7, 8, 12].

## 2.2 Ionothermal synthesis

Thomas and co-workers reported an ionothermal synthesis strategy to produce COFs [13, 14]. The cyclotrimerization of aromatic nitrile building units in molten  $\text{ZnCl}_2$  at  $400^\circ\text{C}$  affords porous covalent triazine-based frameworks (CTFs), a special class of COFs, with robust chemical and thermal stabilities. Molten  $\text{ZnCl}_2$  acts as both the solvent and the catalyst for the reversible cyclotrimerization reaction. Compared with those COFs obtained under solvothermal synthesis method, the CTFs have the disadvantage in crystallinity control because the reversible cyclotrimerization reaction takes place under very harsh reaction conditions. Also, the harsh reaction conditions limit the building block availability. Most synthesized CTFs are amorphous structures that lack long-range molecular order. To date, only two building units have been successfully used to synthesize the crystalline CTFs [13, 14].

Recently, a common ionic liquid, 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ( $[\text{bmim}][\text{Tf}_2\text{N}]$ ) has been used as solvent to prepare highly crystalline COF materials [15]. It is well known that ionic liquids are a class of low-temperature molten salts (with molten point less than  $100^\circ\text{C}$ ) and they are widely regarded as environmentally benign media because they can be used as an alternative to the traditional organic solvents [16]. Ionic liquids are nonvolatile, nonflammable, and their properties can be changed by counter anions. These interesting properties make them very attractive in many important reactions in industrial field. Particular interest has been shown in the preparation of molecular sieves [17] and metal-organic frameworks (MOFs) [18, 19]. Since ionic liquids have a neglectable vapor pressure, this strategy displays significant merits by eliminating any safety concerns associated with high autogenous pressures. Besides, some novel architectures have often been obtained when ionic liquids are used instead [17]. In this regard, Qiu and his co-workers firstly reported the synthesis of several 3D

COFs by using ionic liquids as reaction medium [15]. Crystalline 3D COFs can be obtained under very mild conditions. A high-reaction speed has been observed, for example, 3D-IL-COF-1 can be obtained within only 3 minutes. Furthermore, it was found that the ionic liquid can be reused without obvious activity loss. This work not only provides a new strategy to synthesize COFs but also opens a potential way to green large-scale COF synthesis in industry.

### 2.3 Microwave synthesis

Microwave synthesis is to apply microwave radiation in chemical reactions. Microwave heating is an effective way to accelerate the chemical reactions. This technology has been widely used to synthesize crystalline MOF materials [20]. Microwave heating can possess certain benefits over conventional oven heating, including reaction rate acceleration, milder reaction conditions, higher product yield, lower energy usage, different reaction selectivities, and so on. Therefore, a rapid microwave-assisted method has been reported by Cooper and his co-workers for the synthesis of COF materials [21, 22]. Using microwave heating, both 2D COF-5 and 3D COF-102 can be obtained in 20 minutes, which is much faster than the reaction time of 72 hours required under solvothermal synthesis condition [2, 23]. Moreover, microwave heating affords a BET surface area of  $2019 \text{ m}^2 \text{ g}^{-1}$  for COF-5, which is slightly higher than that synthesized solvothermally ( $1590 \text{ m}^2 \text{ g}^{-1}$ ).

### 2.4 Properties of COFs

The most important concern of porous materials is porosity. For traditional crystalline porous materials, like zeolite, structure-directing agents are generally used to template the formation of porous structure. The formation mechanism of COFs has been rarely reported, but it is generally accepted that the building blocks are first condensed into oligomers, which is similar to the step-growth of crystallization. Then, a nucleation process may afford metastable polymers or templated polymers. The small oligomers were further grown through the persistent linkage and stacking of building blocks, and simultaneously, the defects of amorphous polymers were repaired by a broken and reformed process, until the crystals achieve the bulk ascertained by X-ray diffraction, affording an extended crystalline porous structure with high surface area [24]. The molecular structure of building blocks governs the porosity of COFs. The length of building blocks determines the pore size of COFs, and the geometrical shape determines the topological structures of COFs, which has been shown in **Figure 3**. The designability of COFs in porosity is a distinct difference from inorganic zeolites. The COFs with porosity in different sizes and shapes have been widely reported and will not be discussed here.

The surface areas of COFs are comparable to those of MOFs, but are generally larger than those of zeolites. The earliest reported COF-1 and COF-5 exhibited a surface area of  $S_{\text{BET}} = 711 \text{ m}^2 \text{ g}^{-1}$ ; the pore volume  $V_p = 0.32 \text{ cm}^3 \text{ g}^{-1}$  (**gra**, P6<sub>3</sub>/mmc) for COF-1 and the surface area of  $S_{\text{BET}} = 1590 \text{ m}^2 \text{ g}^{-1}$ ; and the pore volume  $V_p = 0.998 \text{ cm}^3 \text{ g}^{-1}$  (**bnn**, P6/mmc) for COF-5 [2]. The subsequently reported 2D COF-6, COF-8, and COF-10 demonstrated the surface areas of  $S_{\text{BET}} = 1049, 968,$  and  $976 \text{ m}^2 \text{ g}^{-1}$  and the pore volume  $V_p = 0.32, 0.69,$  and  $1.44 \text{ cm}^3 \text{ g}^{-1}$ , respectively [25]. Dichtel et al. [26] used different sized building blocks to construct COFs. The condensations of Zn phthalocyanine (ZnPc) with pyrene diboronic acid, diphenyl butadienediboronic acid, naphthalenediimide diboronic acid, and PPE diboronic acid afford COFs with pore sizes of 2.7, 3.4, 4.0, and 4.4 nm, respectively. For 2D COFs, the surface areas of COFs are generally in the range from several hundreds to over  $1000 \text{ m}^2$  per gram. However, a 2D mesoporous imine-based ILCOF-1 exhibited



high surface area of  $S_{\text{BET}} = 2723 \text{ m}^2 \text{ g}^{-1}$  and  $S_{\text{Lang}} = 3453 \text{ m}^2 \text{ g}^{-1}$ , respectively [27]. This is the largest value reported to date for 2D COFs. In comparison with 2D COFs, 3D COFs possess relatively higher surface areas. Noninterpenetrated COF-105 (**ctn**) and COF-108 (**bor**) have surface areas of 3472 and 4210  $\text{m}^2 \text{ g}^{-1}$ , respectively [23]. The interpenetrated structures are inclined to reduce the surface area of in 3D COF nets. COF-300 with four- or fivefold interpenetration (**dia**) affords a surface area of  $S_{\text{BET}} = 1360 \text{ m}^2 \text{ g}^{-1}$  [28], and COF-320 with ninefold interpenetration **dia** net gives a surface area of  $S_{\text{Lang}} = 2400 \text{ m}^2 \text{ g}^{-1}$  [29], which is obviously lower than those of noninterpenetrated COF-105 and COF-108. Recently, a 3D COF with a record high surface area was reported by McGrier's group [30]. The linkage of  $\pi$ -electron-conjugated dehydrobenzoannulene and tetrahedraltetra-(4-dihydroxyborylphenyl)methane produced 3D DBA-3D-COF 1. This COF achieves a surface area of  $S_{\text{BET}} = 5083 \text{ m}^2 \text{ g}^{-1}$ , a highest value among all COFs. Even though the COF was metalated with Ni, only a slight reduction in the surface area was observed and Ni-DBA-3D-COF 1 still has a surface area of  $S_{\text{BET}} = 4763 \text{ m}^2 \text{ g}^{-1}$ .

It seems that crystalline porous structure is inclined to provide higher surface area than amorphous materials. 3D COF-DL229, constructed by  $T_d$ -symmetric 1,3,5,7-tetrakis(4-aminophenyl)-adamantane and (TAPA) and 1,4-phthalaldehyde (PTA) by our group, shows a BET surface area of 1762  $\text{m}^2 \text{ g}^{-1}$  (Langmuir surface area of 1924  $\text{m}^2 \text{ g}^{-1}$ ) [11]. Due to the organic component of COFs in nature, the skeleton of the COF-DL229 is "soft," and thus, the adsorption of vapor iodine within the pores of the COF led to the distortion of the skeleton. The XRD result indicated that the crystalline structure was destroyed, but the linkages were not broken by the captured iodine. The BET surface area of COF-DL229 was greatly decreased from 1762 to 87  $\text{m}^2 \text{ g}^{-1}$ , suggesting that the ordered crystalline structure of COFs afford a higher surface area than their corresponding amorphous counterparts.

### 3. Gas adsorption and storage

As a class of crystalline porous materials, COFs allow the atomically precise integration of pure organic units to create predesigned skeletons and nanopores based on reticular chemistry [3, 4]. Since the landmark work of Yaghi in 2005 [2], COFs have attracted extensive interest and have become one of the fastest growing fields in both material science and chemistry during the past decade. By far, a diversity of functional COF materials (either 2D or 3D structures) with tailored functionalities has been obtained. With tunable chemical and physical properties, these COF materials have been widely applied in various fields, such as in gas storage, photoelectricity, catalysis, etc.

COFs are composed of light elements linked by reversible covalent bonds to form porous materials with high surface areas. Therefore, COFs can be regarded as ideal materials for gas storage. The research of storage capabilities of COFs has mainly focused on hydrogen, methane, and carbon dioxide adsorption. Generally speaking, the gas adsorption performance of a COF material mainly depends on its components and topological structure. In comparison with 3D COFs, the dense  $\pi$ -stacking layer structure of 2D COFs gives rise to limited surface areas and small pore volumes [31], which restricts their potential for gas adsorption. By contrast, 3D COFs possess not only extremely high surface areas but also extraordinarily low densities, and furthermore, the entire material is accessible for adsorbed molecules to "sees" all the atoms of the framework [32]. Such impressive characteristics of 3D COFs make them promising candidates for adsorbent materials. As a result, 3D COFs possess significantly higher uptake capacities than 2D COFs. In this field, more theoretical simulation has been introduced to model the storage capacity of COFs [33, 34].



### 3.1 Hydrogen gas

Due to clean combustion and high chemical energy density, hydrogen has been pursued as an ideal substitute for traditional fossil fuels. The attempt to store hydrogen with COF materials has been recently reported. COF-18 Å (with a BET surface area of  $1263 \text{ m}^2 \text{ g}^{-1}$ ) shows a hydrogen uptake of 1.55% at 1 bar and 77 K [35]. However, COF-11 Å with a lower BET surface area of  $105 \text{ m}^2 \text{ g}^{-1}$  shows a hydrogen uptake of 1.22% under the same conditions. A 2D CTC-based COF, CTC-COF, with mesoporous structure, has been synthesized through solvothermal reaction. CTC-COF shows a surface area of  $1710 \text{ m}^2 \text{ g}^{-1}$  due to its bowl-shaped building block structure, which is larger than its analogue, COF-5 constructed by planar subunits. This material has a hydrogen uptake of 1.12 wt% at low pressure (1.05 bar) [36]. As expected, 3D COFs exhibited a better hydrogen uptake capability than 2D COFs. COF-102 shows a high hydrogen uptake of 7.24 wt% at saturation (35 bar, 77 K) [37], which is even higher than that of amorphous PAF-1 (7.0 wt%) [38]. NTU-COF-2, constructed by two kinds of reversible covalent binds, shows  $\text{H}_2$  uptake as high as  $174 \text{ cm}^3 \text{ g}^{-1}$  (1.55 wt%) at 1.0 bar and 77 K, which makes it a top COF material for  $\text{H}_2$  adsorption reported by far [39]. In 2012, Yaghi and his co-workers reported that a new COF-301-PdCl<sub>2</sub> reaches 60 g/L (100 bar), which is higher than the DOE 2015 target (40 g/L) and close to the ultimate target (2050) of 70 g/L [40]. At 1.0 bar, ILCOF-1 stores moderate amounts of hydrogen (1.3 wt%, 77 K), though it has a high BET surface area of  $2723 \text{ m}^2 \text{ g}^{-1}$  [27]. Compared with experimental research, more theoretical work has been developed to evaluate the interaction of hydrogen gas with the COF pores [32, 41–44].

### 3.2 Methane gas

Methane is another important energetic gas. However, due to the lack of an effective, economic, and safe on-board storage medium, the development of methane-driven automobiles is greatly limited. 3D COF-102 shows a methane storage capacity of  $187 \text{ mg g}^{-1}$  (the target value for methane storage set by the DOE is  $180 \text{ cm}^3$ ), and 3D COF-103 demonstrates a high adsorption capacity of  $175 \text{ mg g}^{-1}$  at 35 bar and 298 K [37], which are comparable to the highest observed values for MOFs (for instance, MOF-210;  $220 \text{ mg g}^{-1}$ ) [45]. In contrast, 2D COFs, including COF-1, COF-5, COF-6, COF-8, and COF-10, show methane storage capacity of 40, 89, 65, 87, and  $80 \text{ mg g}^{-1}$ , respectively, under the same conditions [37]. Similar to hydrogen storage, 3D COFs demonstrated higher storage capability than 2D COFs. By using a multiscale theoretical method, Cao and his coworkers calculated the storage capacities of methane in 3D COFs and their corresponding Li-doped COF materials at 243 and 298 K, respectively [46]. They predicted that at 298 K and 35 bar, COF-102 and COF-103 have excess gravimetric capacities of 17.72 and 16.61 wt%, respectively, which correspond to 302 and  $285 \text{ cm}^3 \text{ (STP)/g}$ . It was shown that the predicted results are in agreement with the experimental ones. Goddard, III et al. designed 14 COFs expected to adsorb large amounts of methane at 298 K and up to 300 bar. They calculated the delivery uptake using grand canonical Monte Carlo (GCMC) simulations and found that among these COF materials, COF-103-Eth-trans and COF-102-Ant exceed the DOE target of  $180 \text{ v(STP)/v}$  at 35 bar for methane storage [47].

### 3.3 Carbon dioxide

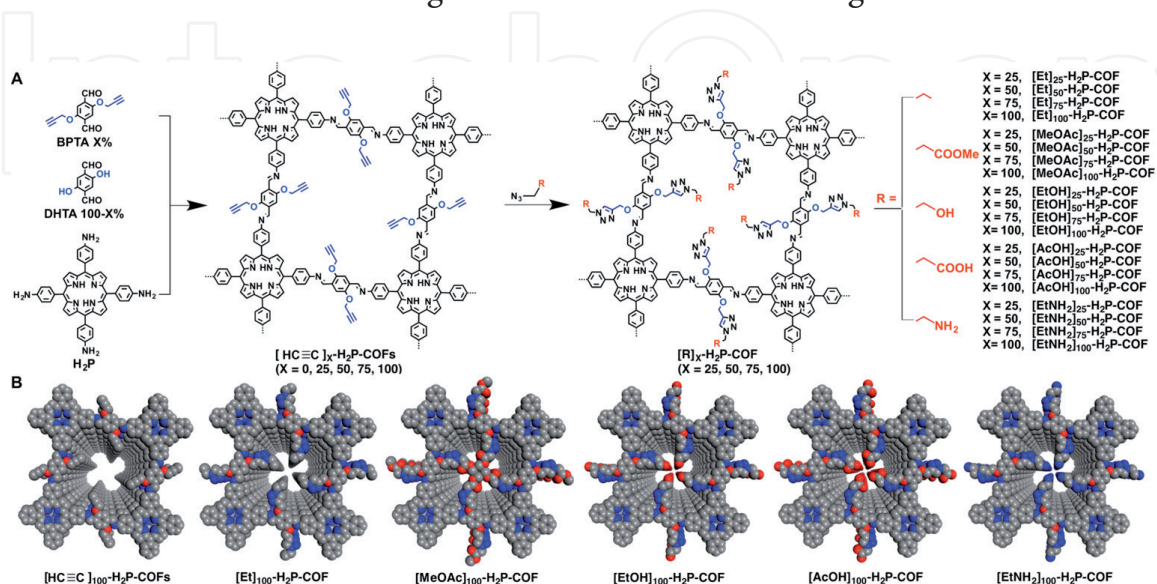
In addition to fuel gas, the adsorption of  $\text{CO}_2$  by COFs has also been intensively investigated. Carbon dioxide is a major greenhouse gas contributing to the global

warming. Over years, capturing CO<sub>2</sub> from industrial emission sources has attracted much interest. COF-1, COF-5, COF-6, COF-8, and COF-10 show CO<sub>2</sub> storage capacity of 230, 870, 310, 630, and 1010 mg g<sup>-1</sup> at 55 bar and 298 K, respectively, and under the same conditions, COF-102 and COF-103 have higher adsorption capability of 1200 and 1190 mg g<sup>-1</sup>, respectively [35]. Jiang et al. designed a series of 2D COFs for CO<sub>2</sub> capture and found that TFPA-TAPB-COF with three triarylamine units in the hexagonal pore showed greatly enhanced CO<sub>2</sub> adsorption capacities (33 mg g<sup>-1</sup>, 1 bar, 298 K and 61 mg g<sup>-1</sup>, 1 bar, 273 K, respectively), which are 2.5-fold those of TFPB-TAPB-COF [48]. They also developed a series of imine-linked COFs with content-tunable, accessible, and reactive ethynyl groups on the walls of COFs (**Figure 4**). These COFs present an ideal platform for pore surface engineering aimed at anchoring desired functional groups with controllable contents [49]. Their results indicated that the anchoring of amino groups led to an overall increase in CO<sub>2</sub> adsorption. Among these COFs, [EtNH<sub>2</sub>]<sub>50</sub>-H<sub>2</sub>P-CO exhibited the highest CO<sub>2</sub> adsorption capability of 157 mg g<sup>-1</sup> at 1 bar and 273 K. The introduction of basic moiety in COFs significantly increases the CO<sub>2</sub> adsorption capacity.

Using the same surface engineering strategy, they further use a conventional imine-linked 2D COF ([HO]<sub>X%</sub>-H<sub>2</sub>P-COF) as a scaffold with porphyrin at the vertices and phenol units on the pore wall of the COFs [31]. A quantitative ring opening reaction between the phenol groups and succinic anhydride decorates the 1D walls with carboxylic acid groups. A series of [HO<sub>2</sub>C]<sub>X%</sub>-H<sub>2</sub>P-COFs with controlled carboxylic acid density was obtained. Functionalization of the channel walls with carboxylic acid groups triggers microporosity in [HO<sub>2</sub>C]<sub>X%</sub>-H<sub>2</sub>P-COFs, and the CO<sub>2</sub> adsorption capability was increased due to strong dipolar interaction of carboxylic acid groups with CO<sub>2</sub> [31]. Besides, an azine-linked COF, ACOF-1, with high levels of nitrogen and high surface area (1176 m<sup>2</sup> g<sup>-1</sup>), can store up to 177 mg g<sup>-1</sup> of CO<sub>2</sub> at 1 bar and 273 K [50].

### 3.4 Iodine vapor

Nuclear power has high energy density and is gradually becoming into one of the pillars of energy sources in the world. However, disposal of the inevitable nuclear waste generated from nuclear fission still remains great challenges. In this regard, <sup>129</sup>I and <sup>131</sup>I are one of the most dangerous wastes because of its long radioactive half-life



**Figure 4.**  
 (a) Schematic of pore surface engineering of imine-linked COFs with various functional groups via click reactions and (b) pore structures of COFs with different functional groups (reproduced from ref. [49], with permission).

( $1.57 \times 10^7$  years), high volatility, and adverse effects on human being and the environment [51]. Therefore, a complete removal of iodine from wastes is essential for eradicating the long-term pollution. In recent years, the capture of radioactive iodine by using porous materials has attracted much attention. Design of porous materials with high iodine capture capacity holds the key to the innovative technology. Various porous materials, like porous organic cages [52], MOFs [53, 54], activated carbon [55], and porous organic frameworks (POFs) [56, 57] have been studied for iodine adsorption. Although some of them have high surface areas, most of them still exhibit low capacity because of their low accessibility of the pores to iodine molecules.

As a new class of emerging porous materials, the capture of iodine with COFs has been recently explored. Zhao's group reported the construction of a new heteropore COF consisting of two different kinds of micropores with unprecedented shapes [58]. The hollow microspheres were observed for the COF, which led to an extremely high volatile iodine uptake (up to 481 wt%), because iodine can be encapsulated within both the inner cavities of hollow microspheres and the porous shells of the microspheres. In addition to 2D COFs, the capture of iodine by 3D COF has been studied by our group. We designed and synthesized a 3D COF, COF-DL229, which consists of a diamond topology knotted by adamantane units [11]. An eightfold interwoven diamond net with 1D channel structure has been obtained, and the extended  $\pi$ -conjugated linkers are laid on the plane of the rings to form the channel walls. This unique arrangement allows a full exposure of all diphenylamine units to the channels. Our experiments showed that COF-DL229 achieved an uptake capacity of 82.4 wt%, corresponding to an adsorption capability of 4.7 g/g in equilibrium at 75°C. Such high iodine capture capability can be attributed to 1D open channel structure,  $\pi$ -conjugated pore walls that form charge transfer complex with iodine, as well as high surface area of COF-DL229 [11].

### 3.5 Ammonia

Liquid ammonia is difficult to handle due to its toxicity and corrosiveness. Searching for an adsorbent for efficient storage of ammonia is therefore of significance to solve this problem. A boron-containing COF, COF-10, has exhibited exceptionally high ammonia uptake (15 mol kg<sup>-1</sup>, 298 K, 1 bar) in comparison with other porous materials [59]. This is higher than other adsorbents. For instance, 13X zeolite has a storage capability of 9 mol kg<sup>-1</sup>, and Amberlyst 15 exhibits a storage capability of 11 mol kg<sup>-1</sup> and MCM-41 shows an adsorption capability of 7.9 mol kg<sup>-1</sup> [60]. Importantly, the captured ammonia can be easily removed only by a simple heating under vacuum.

## 4. Catalysis

All COFs show an open network structure, which offers accessible channels or nanopores with uniform sizes ranging from angstroms to nanometers for guest molecules. This unique structure is special attractive for catalysis applications. In addition, the organic skeletons of COFs make it easy to be decorated with functional groups. For example, unique optical [61, 62] and optoelectronic [63] properties have been endowed to COFs upon decoration of corresponding functional groups. In particular, the assembly of COFs can be achieved by various designable building blocks, which results in innumerable structural topologies and diversified porosities. High surface area, structural versatility, open channels, and easy modification of COFs make them ideal materials used as catalysts. Compared with traditional activated carbon and zeolites, the “designable” assembly of building blocks enables the



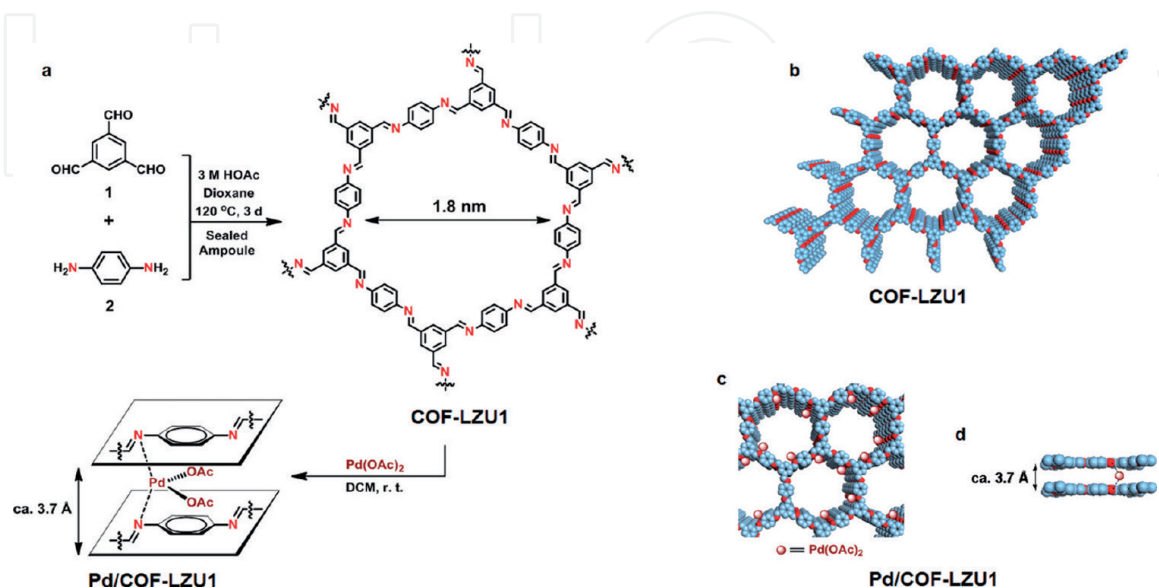
spatial separation of multiple catalytic sites in the framework, endowing COFs with cooperative catalysis character and thus enhanced catalyst reactivity [64]. Using COFs as catalysts is a rapidly developing research field. In the following section, we present the recent advances in catalytic COF materials based on the type of catalytic sites, including single functional active sites, bifunctional active sites, and metal nanoparticles (NPs) embedded in pores of COF catalysts. Catalysis using 3D COFs was also discussed separately. The deliberate or incidental synthesis strategies, the stability, the heterogeneity, and the shape/size selectivity of COF catalysts are mainly presented. It is noted that although COFs have also been applied to photocatalytic and electrocatalytic reactions, we do not discuss in this chapter.

#### 4.1 COFs with single functional group

Due to the fact that COFs are composed of organic components, COFs can be easily decorated with molecular catalysts that acquire activities and/or selectivities comparable to their homogeneous analogues. In general, two strategies have been mainly used to construct catalytically active COFs [65]. One strategy involves the postsynthetic integration of catalytic sites into a COF skeleton. With this method, crystalline COFs are firstly synthesized and catalytic sites are then linked within the pores of COFs through chemical reactions. This postsynthetic modification approach can reduce the damage of COF crystallinity due to bulky catalytic sites embedded. The undesired effect of harsh solvothermal conditions on the catalytic sites can also be avoided. So far, this is the most common way to modify COFs. Another one is the bottom-up strategy that uses building blocks bearing catalytic sites to directly construct COFs. However, if a bulky catalytic site is chosen to attach to building blocks, it will be difficult to obtain highly crystalline COFs.

A pioneer work using COFs as catalysts was reported by Wang and co-workers in 2011 [66]. They developed a 2D imine-linked COF, COF-LZU1, and the eclipsed layered-sheet arrangement of the COF gives the distance of eclipsed nitrogen atoms in adjacent layers as  $\sim 3.7$  Å, which provides an ideal distance for incorporating a variety of metal ions (**Figure 5**).

Pd(II) was embedded into COF-LZU1 through the coordination with nitrogen atoms. The resultant Pd/COF-LZU1 exhibited high catalytic activity for



**Figure 5.** (a) Schematic of the synthesis of COF-LZU1 and Pd/COF-LZU1. Proposed structures of (b) COF-LZU1 and (c, d) Pd/COF-LZU1 possessing regular microporous channels, simulated with a 2D eclipsed layered-sheet arrangement (reproduced from ref. [66], with permission).

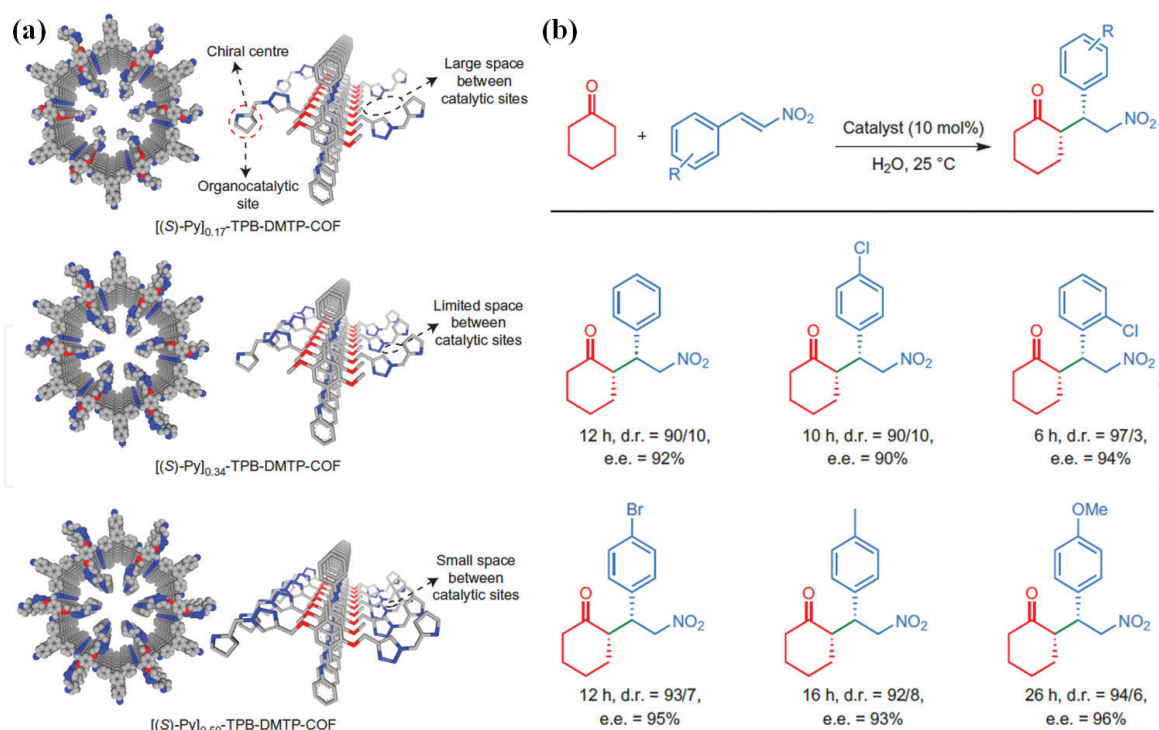


Suzuki-Miyaura coupling reaction. The authors believe that the unique structure of Pd/COF-LZU1 provides efficient access to the catalytic sites and fast mass-transport of the reactants/products, which led to its superior activity in catalyzing the Suzuki-Miyaura reaction. Furthermore, high stability and easy recyclability have also been observed for the catalyst. In a similar fashion, Chen et al. successfully incorporated copper ions ( $\text{Cu}^{2+}$ ) into 2D TAPT-DHTA-COF, in which the hydroxyl groups on the building block can coordinate with  $\text{Cu}^{2+}$  in combination with imine linkers [67]. The catalytic performances of the resultant  $\text{Cu}^{2+}$ -containing COFs, termed Cu-COFHX and Cu-COFDMF, have been studied and both COFs exhibited high reactive activity toward selective oxidation of styrene to benzaldehyde. In a similar way,  $\text{Pd}^{2+}$  ions have been successfully loaded within the layers of COFs through the coordination with either bipyridyl or porphyrin group [68, 69]. The excellent catalytic activity has been observed for the Heck reaction and Suzuki coupling reaction, respectively. In addition, a simple two-step bottom-up synthetic strategy was used to synthesize the molybdenum-doped COF. The as-synthesized Mo-COF was found to be highly active in catalyzing a series of selective oxidation reactions [70]. Based on the principle of reticular chemistry, a new COF, CPF-2, was synthesized through the condensation of 2D four-branched tetraphenylamine porphyrin (TAPP) and the 2D trigonal 1,3,5-triformylbenzene (TFB) [71]. Although X-ray diffraction (XRD) results show that CPF-2 is a crystalline material, the crystal structure is not successfully resolved. Even so,  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  were successfully coordinated within the porphyrinic framework of CPF-2. The Co(II)-doped material Co-CPF-2 shows high efficiency in heterogeneous catalysis of the aerobic epoxidation of olefins under mild conditions, in which a high conversion (>99%) and epoxide selectivity (93%) have been achieved for the aerobic epoxidation of styrene.

In addition to metal ions, organocatalytic moieties have been introduced into COFs. Jiang's group has performed a series of work to attach organocatalytic sites into COFs. A pore surface engineering strategy was used to modify the properties of COFs. This strategy realizes the control over the number and composition of catalytic sites on the channel walls of COFs, thus providing a basic design principle for the preparation of catalytic COFs. In 2014, they utilized a mesoporous imine-linked porphyrin COF as a scaffold, in which the porphyrin units are located at the vertices and the phenyl groups occupy the edges of tetragonal polygon frameworks [72]. A series of  $[\text{HC} \equiv \text{C}]_x\text{-H}_2\text{P-COFs}$  with different alkynyl densities was obtained. Catalytic active pyrrolidine units were then integrated into the pore walls of the  $[\text{HC} \equiv \text{C}]_x\text{-H}_2\text{P-COFs}$  through click reaction. The catalytic activities of  $[\text{Pyr}]_x\text{-H}_2\text{P-COFs}$  in a Michael addition reaction in aqueous solutions were investigated. It is shown that the COF catalyst features enhanced activity, broad applicability, good recyclability, and high capability under continuous-flow conditions.

They subsequently reported stable COFs,  $[\text{HC} \equiv \text{C}]_x\text{-TPB-DMTP-COFs}$ , with adjustable acetylene density [73]. Anchoring chiral centers and organocatalytic sites onto the channel walls of  $[\text{HC} \equiv \text{C}]_x\text{-TPB-DMTP-COFs}$  was then carried out through click reaction, and chiral organocatalytic  $[(S)\text{-Py}]_x\text{-TPB-DMTP-COFs}$  were obtained. In these COFs, each hexagonal macrocycle can have one, two, or three (S)-Py units on average. The organocatalytic sites were integrated into the walls to offer catalytic nanospaces of different sizes (**Figure 6a**). It is found that Michael reactions can be conducted in neat water under mild conditions (25°C and 1 bar), and a 100% conversion, with high isolation yield and high enantioselectivity and diastereoselectivity, has been observed for the addition reaction of cyclohexanone and  $\beta$ -nitrostyrene. This outstanding catalytic performance has also been expanded to different  $\beta$ -nitrostyrenes, illustrating the generality of the catalyst (**Figure 6b**).

Recently, Cui and co-workers have carried out a series of work that used COFs as catalysts. A multivariate strategy was first used to construct chiral COFs. The chiral

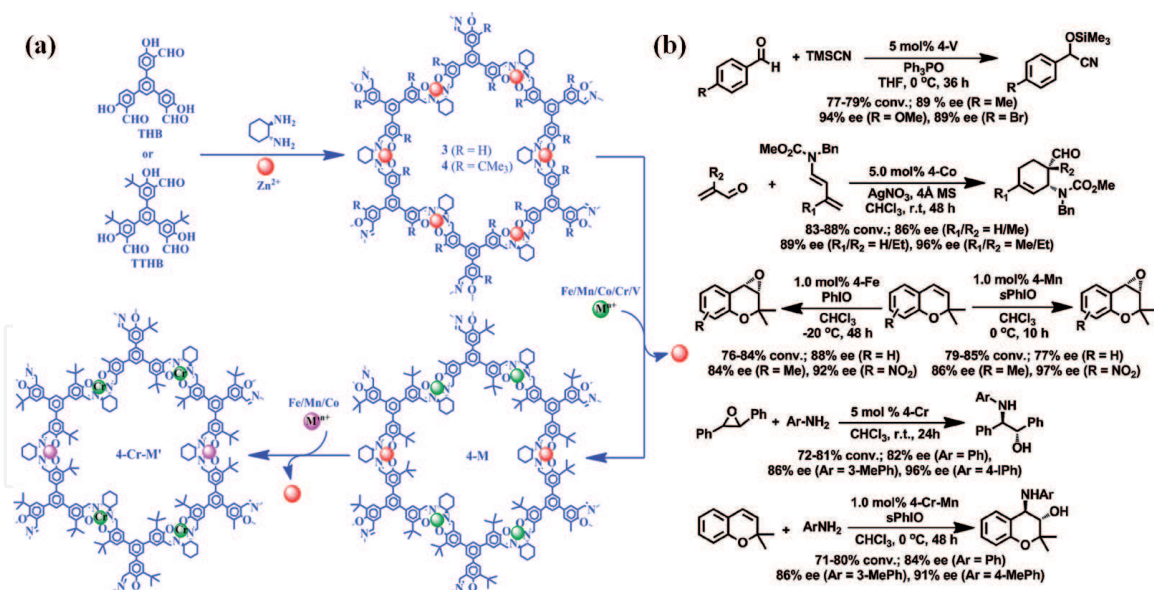


**Figure 6.**

(a) Channel-wall structure of the chiral organocatalytic COFs. The open structures of the chiral centers and the catalytic sites on the channel walls are shown for different COFs. (b) Scope of reactants. Different  $\beta$ -nitrostyrene derivatives investigated for the Michael reactions catalyzed with chiral COFs, their products, e.e. yields and d.r. values. R, substituent H, Cl, Br, me, or OMe (reproduced from ref. [73], with permission).

COFs exhibit high crystallinity and good stability and thus are used as catalysts for asymmetric catalysis [74]. These 2D chiral COFs showed high catalytic activity in catalyzing asymmetric aminooxylation reaction, aldol reaction, and Diels-Alder reaction. The stereoselectivity and diastereoselectivity for the reactions are found to be comparable to or surpassing their corresponding homogeneous counterparts. A metal-directed synthesis strategy has also been developed by Cui's group, in which chiral Zn(salen)-based COFs have been obtained by the imine-condensations of enantiopure 1,2-diaminocyclohexane and  $\text{C}_3$ -symmetric tris(acylaldehydes) with one or no 3-tert-butyl group (Figure 7a) [75]. Metal ions can be loaded within the Zn(salen) modules of the COFs by using an ion exchange process. The loading of metals did not change high crystallinity and porosity of the COF. The catalytic performance of the resultant COFs was detected by a series of reactions, including asymmetric cyanation of aldehydes, Diels-Alder reaction, alkene epoxidation, and epoxide ring-opening reaction. The excellent catalytic activity and selectivity have been observed for these reactions (Figure 7b).

Very recently, they also demonstrated that chiral COFs can be prepared from achiral organic precursors by chiral catalytic induction. Nine 2D chiral COFs were synthesized under solvothermal conditions by the imine condensations of 1,3,5-triformylphloroglucinol (Tp) and diamine or triamine linkers in the presence of catalytic amount of (R)- or (S)-1-phenylethylamine [76]. Using CCOF-TpTab as a heterogeneous catalyst, high reactive activity has been observed in catalyzing asymmetric Henry reaction. In this respect, our group has successfully introduced ionic liquids into the COF framework by using a postsynthetic strategy [77]. The immobilization of ionic liquids onto Py-COFs was directly accomplished through the Williamson ether reaction between the phenol group in  $[\text{HO}]_{x\%}\text{-Py-COFs}$  and (2-bromoethyl)triethylammonium bromide ionic liquid. Among these COFs,  $[\text{Et}_4\text{NBr}]_{50\%}\text{-Py-COF}$  showed a strong  $\text{CO}_2$  adsorption capability of  $164.6 \text{ mg g}^{-1}$  at 273 K and 1 bar. The catalytic transformation of  $\text{CO}_2$  into formamides was detected



**Figure 7.**

(a) Synthesis of the chiral COFs. (b) Asymmetric reactions catalyzed by the CCOFs (reproduced from ref. [75], with permission).

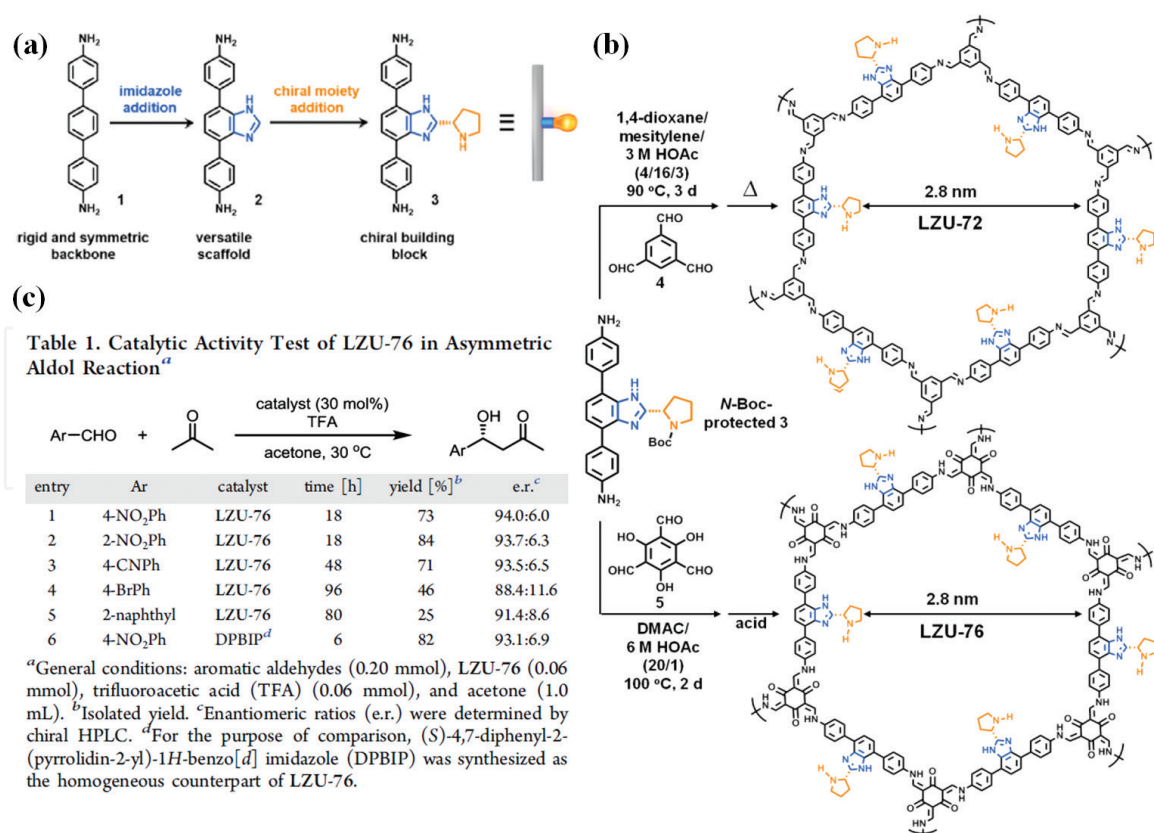
and the [Et<sub>4</sub>NBr]<sub>50%</sub>-Py-COF showed high catalytic activity even if the reaction was carried out at ambient temperature and pressure. We believe that the enrichment of CO<sub>2</sub> into the COF nanopores may lead to its outstanding catalytic ability.

Using a bottom-up strategy to construct functional COFs is relatively difficult because it must simultaneously satisfy requirement of crystallinity and functionality. So far, only several attempts have shown to be successful for the synthesis of catalytic COFs. A facile strategy for the direct construction of chiral-functionalized COFs using chiral (S)-4,4'-(2-(pyrrolidin-2-yl)-1H-benzo[d]imidazole-4,7-diyl) dianiline (**Figure 8a**) as a building block has been achieved by Wang and co-workers [78]. Two chiral COFs, LZU-72 and LZU-76, were prepared based on this chiral building block (**Figure 8b**). Their results showed that these two COFs are structurally robust and highly active as heterogeneous organocatalysts. LZU-76 can catalyze asymmetric aldol reaction to produce the corresponding products with excellent enantioselectivity (88.4:11.6–94.0:6.0 e.r.) (**Figure 8c**).

A sulfonated building block, 2,5-diaminobenzenesulfonic acid, was also used to construct an acidic COF, termed TFP-DABA, together with 1,3,5-triformylphloroglucinol [79]. The as-synthesized TFP-DABA was found to be a highly efficient catalyst for fructose conversion. The remarkable yields (97% for 5-hydroxymethylfurfural (HMF) and 65% for 2,5-diformylfuran), good chemoselectivity and recyclability have been observed for this catalyst. Cui and co-workers [80] reported the synthesis of two chiral COFs (CCOF-1 and CCOF-2) by direct condensations of enantiopure TADDOL-derived tetraaldehydes with 4,4'-diaminodiphenylmethane (4,4'-DADPM). After optimization of the reaction conditions, CCOF-1 in the presence of excess Ti(OiPr)<sub>4</sub> was found to be highly active for the addition reaction of Et<sub>2</sub>Zn to aromatic aldehydes to produce secondary alcohols.

In some cases, COFs themselves can serve as efficient catalysts for some reactions. CTFs are a special class of COFs constructed through the reversible ionothermal trimerization of aromatic nitriles. The inherent basic feature of triazine materials means that they can be used as basic catalysts. The efficient catalytic activities of the high-surface-area triazine frameworks have been clearly demonstrated in the cycloaddition of CO<sub>2</sub> to epichlorohydrin [81]. Besides, Jiang and co-workers [82] found that a  $\pi$ -electronic COF can serve as heterogeneous catalyst. The use of 1D  $\pi$ -walls as catalytic beds can facilitate the reaction of Diels-Alder





**Figure 8.**

(a) Design of chiral building block. (b) Synthesis of chiral LZU-72 and LZU-76. (c) Catalytic activity test of LZU-76 in asymmetric aldol reaction (reproduced from ref. [78], with permission).

reactions. Their result indicated that the reaction can proceed effectively at room temperature and at 1 bar.

## 4.2 COFs with bifunctional reactive sites

It is of great interest to combine two different active sites in one substrate as in many cases, the reaction can be facilitated remarkably, especially for cascade/tandem/one-pot reactions. However, there still remains a challenge to design bifunctional catalysts. Up to now, only few such systems of this sort have been reported.

The first successful incorporation of bifunctional catalytic sites in the crystalline porous COF (2,3-DhaTph) was developed by Banerjee et al. [83]. They report the synthesis of a bifunctional catechol-porphyrin COF, containing both acidic and basic sites, which can act as a heterogeneous catalyst for one-pot acid-catalyzed deprotection of acetal groups followed by base-catalyzed Knoevenagel condensation reaction. The reaction of benzaldehyd dimethylacetal with malononitrile in a mixture of toluene and water at 80°C gives the desired 2-benzylidenemalononitrile product with an excellent isolated yield of 96% in the presence of 2,3-DhaTph. Our group used 2,2-bipyridyl-5,5-dialdehyde (2,2'-BPyDCA) as building blocks to construct a series of 2D imine-based 2D COFs (X% BPy COF) [84]. It is known that imine at the layers of 2D COFs can provide nitrogen atoms to coordinate with metal ions [66]. This means that X% BPy COFs contain two different types of ligands, namely imine and bipyridine in one COF. Through a programmed synthetic procedure, big-sized Rh(I) was first coordinated with bipyridine on the walls of the COFs and Pd(II) was then coordinated with the nitrogen atoms of the imine within the layers of X% BPy COFs. The resultant bimetallic Rh<sup>I</sup>/Pd<sup>II</sup>@X% BPy COFs were used as catalysts for a cascade reaction. The reaction of phenylboronic acid with benzaldehyde gives a final product of benzophenone. Our investigation has revealed



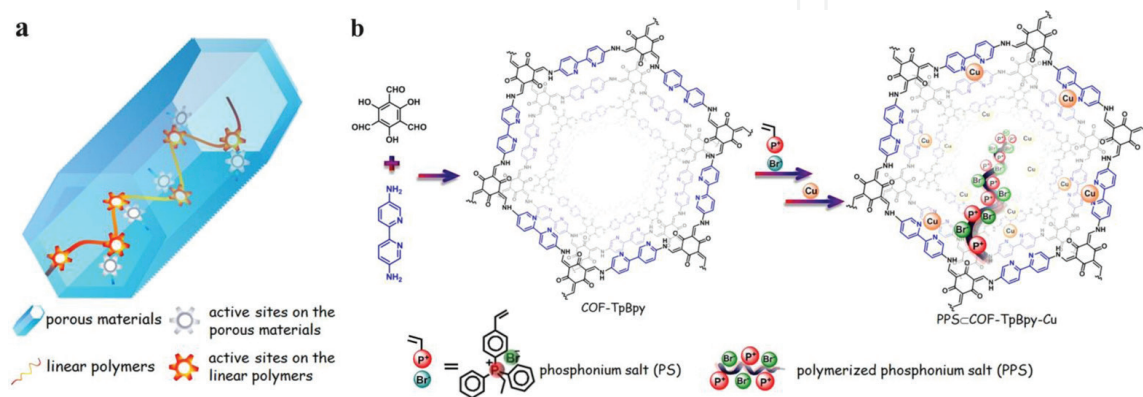
that  $\text{Rh}^{\text{I}}$  catalyzed the addition reaction of phenylboronic acid with benzaldehyde to product diphenylmethanol, and the intermediate was then oxidized into benzophenone catalyzed by  $\text{Pd}^{\text{II}}$ . A total 90% isolation yield was obtained, showing an excellent catalytic activity of the bimetallically docked 2D COFs in the one-pot addition-oxidation cascade reaction. The high surface area, controllable metal-loading content, and predesigned active sites make COFs ideal candidates for using as heterogeneous catalysts in a wide range of reactions. In addition, Ma et al. [85] has developed a new strategy to decorate functional active sites into COFs. Surface Lewis acid sites are anchored on the walls of COF-TpBpy through the metalation of  $\text{Cu}^{2+}$  with building blocks, namely bipyridine units, and linear polymers with excellent flexibility are threaded throughout the channels of the COF via *in situ* radical polymerization of ionic monomers (**Figure 9**). Due to the flexibility of linear polymers, it is possible for polymers in close proximity surface Lewis acid sites, which make them easy to cooperate with the co-catalyst,  $\text{Br}^-$ , of the polymers. This special structure can catalyze the cycloaddition of the epoxides and  $\text{CO}_2$  efficiently.

### 4.3 COFs with metal nanoparticles (NPs) entrapped

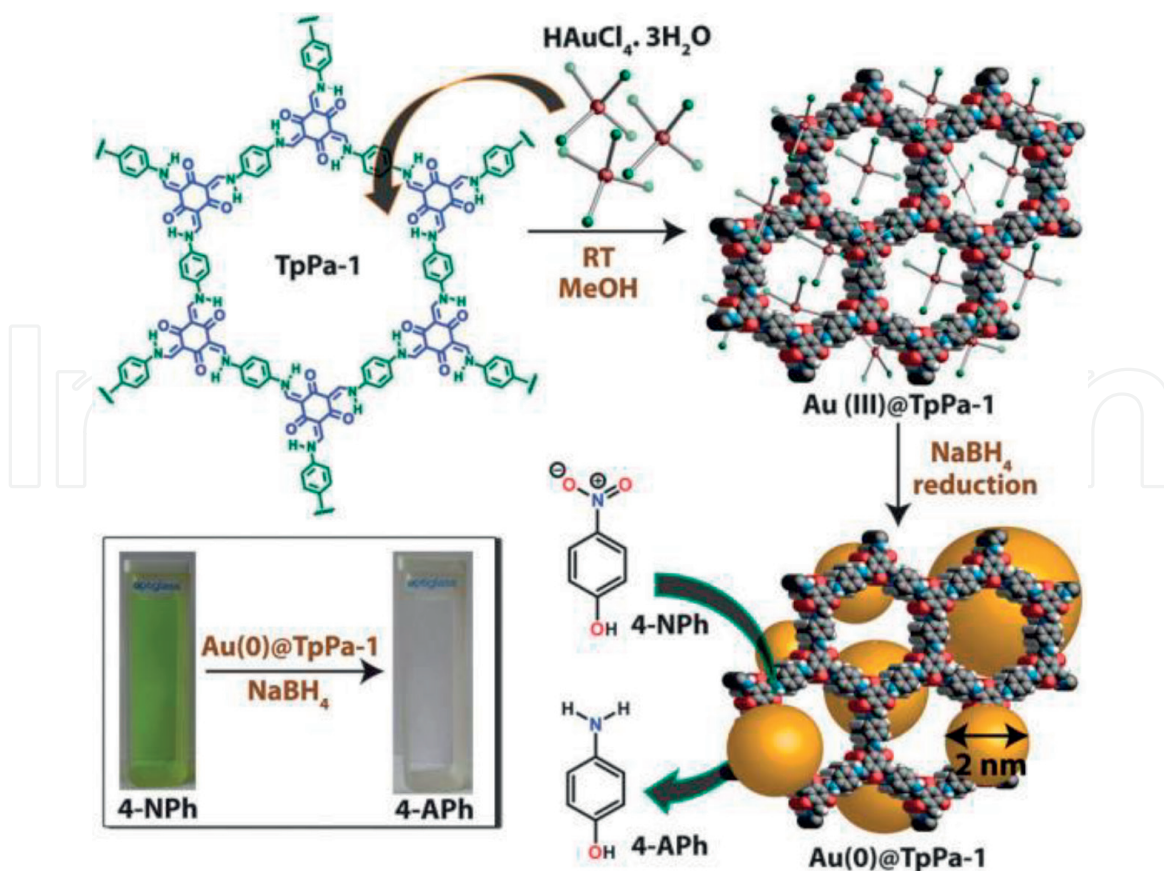
The inherent host-guest chemistry enables the implementation of desired substances by filling the pores with various guest molecules. Metal NPs have demonstrated excellent catalytic activity in many chemical reactions. Therefore, the doping of COFs with metal NPs is of significant interest for application in heterogeneous catalysis. We can predict the advantages of metal NP-loaded COFs:

(1) high surface area of COFs allows for more active sites being embedded, which can facilitate chemical reactions; (2) postsynthetic modification or prior introduction of ligands makes it easy to anchor metal NPs; (3) the pore channels in COFs are well isolated, and thus, the aggregation of entrapped NPs can be hampered and metal NP growth can be confined to an certain extent.

The first example to load metal NPs was carried out by Banerjee and co-workers in 2014 [86]. A highly stable, porous, and crystalline COF (TpPa-1) was first prepared and the  $\text{Au}(\text{0})@\text{TpPa-1}$  catalyst was synthesized via the solution infiltration method (**Figure 10**). The as-synthesized  $\text{Au}(\text{0})@\text{TpPa-1}$  catalyst is stable and shows superior reactivity for nitrophenol reduction reaction. With the same strategy, they further reported the incorporation of  $\text{Pd}(\text{0})$  NPs into the pores of TpPa-1 COF [87]. The as-synthesized  $\text{Pd}(\text{0})@\text{TpPa-1}$  has proven highly active toward the Cu-free Sonogashira, Heck, and sequential one-pot Heck-Sonogashira cross-coupling reactions. The COF is also highly stable under the reaction conditions because of



**Figure 9.** (a) The concept of heterogeneous concerted catalysis between active sites on the porous materials and highly flexible linear polymers and (b) schematic of  $\text{PPS}@\text{COF-TpBpy-Cu}$  synthesis and structures of  $\text{COF-TpBpy}$  and  $\text{PPS}@\text{COF-TpBpy-Cu}$  (reproduced from ref. [91], with permission).



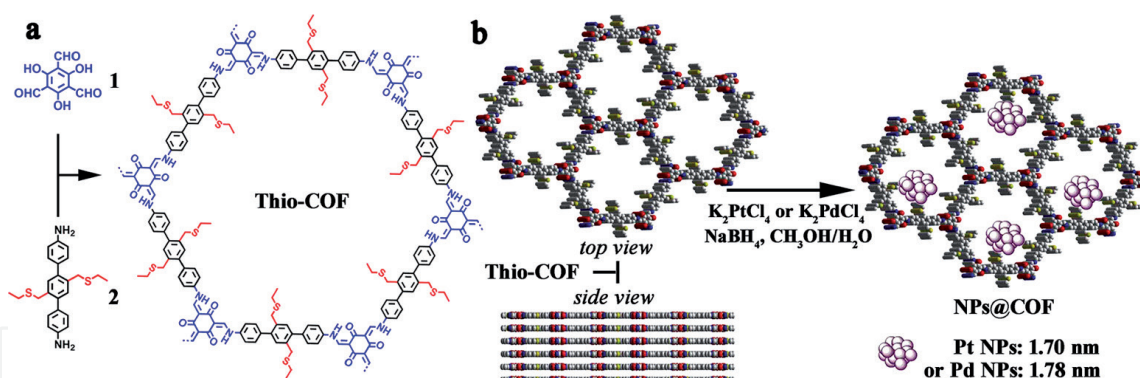
**Figure 10.**

*Synthesis of the  $\text{Au}(0)@\text{TpPa-1}$  catalyst using the solution infiltration method for nitrophenol reduction reaction. Inset image: The optical images of the color change observed for the conversion of 4-nitrophenol to 4-aminophenol after the addition of  $\text{Au}(0)@\text{TpPa-1}$  (reproduced from ref. [86], with permission).*

its negligible metal leaching, nonsintering behavior, and good recyclability. In 2017, they further developed a novel synthetic strategy by choosing a predesigned metal-anchored building block for in situ generation of metal (Pd) NPs in the stable, porous, and crystalline COF without using conventional reducing agents [88]. It was revealed that the breakage of the Pd-N bond of the Bpy-PdCl<sub>2</sub> complex results in the formation of Pd(0) NPs. This hybrid COF is found to be an excellent reusable heterogeneous catalyst for the synthesis of 2-substituted benzofurans from 2-bromophenols and terminal alkynes via a tandem process.

It is of great interest to load metal NPs with desired shape and size into a COF matrix. Such composite has been produced by an encapsulation strategy. The polyvinylpyrrolidone (PVP)-modified Au NPs with desired shape and size have been successfully loaded within the nanopores of TAPB-DMTP COF during its synthesis process [89]. It is revealed that the incorporation of Au NPs does not obviously change the crystallinity and pore structures of the COF matrices. The Au NP-loaded TAPB-DMTP COF displays recyclable catalytic performance for reduction of 4-nitrophenol.

A facile single-step loading of Pd(0) NPs into an amphiphilic triazine COF has been carried out by Vaidhyanathan et al. [90]. The catalytic performance was evaluated by Heck coupling and C-C coupling reactions. The COF catalyst exhibits high catalytic activity and good recyclability for Heck couplings with no sign of catalyst leaching. As an oxidation catalyst, CO was 100% converted to CO<sub>2</sub> at 150°C with no loss of activity with time. Besides, COFs have been found to be ideal templates for the synthesis of ultrafine metal NPs [91]. Both size and dispersity of NPs into COF's matrix could be well controlled. In this regard, a thioether-containing building block has been designed to construct task-specific COF (Thio-COF). The



**Figure 11.**

(a) Synthesis of Thio-COF and (b) schematic representation of the synthesis of Thio-COF supported PtNPs@COF and PdNPs@COF. Top and side views of the energy-minimized models of Thio-COF (yellow, S; blue, N; gray, C; red, O) are shown in (b) (reproduced from ref. [85], with permission).

appearance of thioether confined the growth of metal NPs and the ultrafine NPs (1.70 nm for Pt and 1.78 nm for Pd NPs) were obtained inside the porosity of the COF (**Figure 11**). The excellent catalytic activities have been observed in nitrophenol reduction and Suzuki-Miyaura coupling reaction under mild conditions.

#### 4.4 Catalysis with 3D COFs

In 2014, Yan and co-workers used 3D COFs as catalyst for chemical reactions [92]. Two 3D COFs (BF-COF-1 and BF-COF-2) have been synthesized based on the condensation reaction of 1,3,5,7-tetraaminoadamantane and 1,3,5-triformylbenzene or triformylphloroglucinol. Both BF-COF-1 and BF-COF-2 exhibited high catalytic activity toward Knoevenagel condensation reactions (96% for BF-COF-1 and 98% for BF-COF-2, respectively). Interestingly, the COFs exhibit highly efficient size selectivity due to the pore size of the COFs. For small-sized reactants, like benzaldehyde and malononitrile, the 3D COFs exhibited very good conversion up to 99%, whereas for the large reactants, the reaction proceeded much sluggishly with very poor yield. Constructing COFs by using two different types of reversible covalent bonds has been achieved by Qiu's group [93]. The two linkages, boroxine and imine, provide acidic and basic sites, separately, in one 3D COF material. The double-linked COF can serve as excellent acid-base catalysts for one-pot cascade reactions. The high conversion of 100% for benzaldehyde dimethyl acetal is achieved, and the formed intermediate, benzaldehyde, is reacted through consecutive Knoevenagel condensation with malononitrile to give the final product, benzylidene malononitrile in high yields (98% for DLCOF-1 and 96% for DL-COF-2). Wang et al. described a dynamic 3D COF LZU-301 used as a Lewis-base catalyst for the Knoevenagel condensation between malononitrile and three aromatic aldehydes. An obvious size selectivity effect has been observed for different sized aldehydes [94].

## 5. Outlook and conclusions

Covalent organic frameworks (COFs) represent an emerging class of crystalline porous materials. Owing to their unique structural features and recent interesting exploitation of their properties, these materials undoubtedly show significant potential and advantages in gas storage and separation, catalysis, optoelectricity, and so on. Over the past 10 years, great progress has been made; however, the investigation of COF materials is still in its infancy, and COF chemistry still faces great challenge in practical applications.



A big challenge in the COF synthesis is the exploration of new synthesis strategy. The successful synthesis of crystalline COFs has long been an intractable problem. So far, there is still lack of universal regulation to direct the construction of crystalline COFs. Therefore, there is a clear need to expand the synthetic possibilities in different ways. In-depth understanding of the formation mechanism would provide insightful information for the COF synthesis. In this respect, ionic liquids have been attempted to act as reaction media and exhibited obvious advantage over traditional organic solvents. Given the fact that there are at least a million binary ionic liquids and potentially more than  $10^{18}$  ternary ionic liquids (compared with only about 600 molecular solvents) [17], the use of ionic liquids would open up many new possibilities in the preparation of COF materials with highly periodic and robust frameworks. Furthermore, synthesis of COFs is now limited to the laboratory, and it is also a challenge to synthesize COFs on an industrial scale for prospective practical applications. Also, how to find a new synthetic route to reduce the cost of COFs is also a difficult task and far in the future.

Another challenge in the COF field is the resolution of their crystalline structure. So far, the structure of COFs is expected to be analyzed based on the given PXRD patterns combined with computational simulation technique. However, in many cases, due to the partial crystallinity of COFs, the overall structural regularity is poor. Apart from searching for an effective synthesis route to construct highly crystalline COFs, efforts for the installation of crystalline structural database of COFs might be encouraged. Besides, how to further improve the chemical/thermal stability of COFs so that these materials can be used under very harsh conditions (e.g., strong acidity or alkalinity, high temperature, and high overpotential) is another important aspect that requires rapid development.

So far, most of the reported COFs are 2D layered crystalline structures, i.e., 2D COFs. In comparison with the effects governed by DCC, the  $\pi$ - $\pi$  stacking interaction between layers of 2D COFs is relatively weak to construct highly periodic and porous COF materials. Therefore, it is also of significance to develop more 3D COFs. Take catalytic COFs as an example, it is of interest to design COFs with versatile inner cavities, which can provide active sites on the pore surface and transport reactants/products to or from inner reactive vessels.

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## Conflict of interest

The authors declare no competing financial interest.



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