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## Post-synthetic modifications of covalent organic frameworks (COFs) for diverse applications

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Covalent organic frameworks (COFs) are porous and crystalline organic polymers, which have found usage in various fields. These frameworks are tailorable through the introduction of diverse functionalities into the platform. Indeed, functionality plays a key role in their different applications. However, sometimes functional groups are not compatible with reaction conditions or can compete and interfere with other groups of monomers in the direct synthetic method. Also, pre-synthesis of bulky moieties in COFs can negatively affect crystal formation. To avoid these problems a post-synthetic modification (PSM) approach is a helpful tactic. Also, with the assistance of this strategy porous size can be tunable and stability can be improved without considerable effect on the crystallite. In addition, conductivity, hydrophobicity/ hydrophilicity, and chirality are among the features that can be reformed with this method. In this review, different types of PSM strategies based on recent articles have been divided into four categories: (i) post-functionalization, (ii) post-metalation, (iii) chemical locking, and (iv) host-guest post-modifications. Post-functionalization and chemical locking methods are based on covalent bond formation while in post-metalation and host-guest post-modifications, non-covalent bonds are formed. Also, the potential of these post-modified COFs in energy storage and conversion (lithium-sulfur batteries, hydrogen storage, proton-exchange membrane fuel cells, and water splitting), heterogeneous catalysts, food safety evaluation, gas separation, environmental domains (greenhouse gas capture, radioactive element uptake, and water remediation), and biological applications (drug delivery, biosensors, biomarker capture, chiral column chromatography, and solid-state smart nanochannels) have been discussed.

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### 1. Introduction

Yaghi and co-workers introduced novel porous and crystalline organic polymers for the first time in 2005.<sup>1</sup> These polymers are named covalent organic frameworks (COFs). Since then, this field has attracted the attention of a large number of scientists. Due to the topology and linkage diversity as well as building monomers with different sizes, reactive groups, chiral centers, and docking sites, various COFs have been constructed.<sup>2</sup> Due to their specific attributes, these compounds have found usage in catalysis,<sup>3,4</sup> sensors,<sup>5-7</sup> separation,<sup>8,9</sup> adsorption,<sup>10-13</sup> energy storage,<sup>14-16</sup> drug delivery,<sup>17-20</sup> and electronic devices.<sup>21-23</sup> Functional groups of COFs play a key role in these applications. For the synthesis of functionalized COFs, two approaches are applied: direct and post-modification synthesis.<sup>24</sup> In other words, in pre-synthetic modifications, appropriate functional groups are introduced into the building monomers before the

synthesis of COFs. However, in some cases, anchored molecules are sensitive to COF preparation conditions such as pH or temperature. In some other cases, especially reversible Schiff-base reactions, functionalities such as peripheral amine groups can interfere with the reaction and compete with the targeted amine groups in a condensation reaction. Also, pre-synthesis of bulky moieties in COFs may negatively affect crystal formation. Due to such problems, the direct introduction of functionality may be impossible. Functionality that cannot be directly presented in COFs can be introduced *via* a post-synthetic modification (PSM) approach. By virtue of extremely porous networks and large surface areas of COFs, solvents and reagents can easily get access to reactive points of COFs for post-functionalization.<sup>25</sup> Functionalities can be introduced into the COFs by either covalent bonding or non-covalent bonding. In post-functionalization and chemical locking methods, covalent bonds are formed while in post-metalation and host-guest post-modifications, non-covalent bonds are formed. Also, the physical and chemical properties can be tuned by PSM strategies. Therefore, this method is a promising strategy to synthesize COFs with improved features.

For instance, Jiang *et al.* exerted functionalization through the click reaction of azide-appended building units of the

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## Highlight

initial COF with different alkynes for the synthesis of various triazole-functionalized COFs with tunable surface pore size. Moreover, owing to the different substitutions of triazole moieties, existing on the pore walls, affinity toward gas molecules can be mutable. Specifically, their report was focused on the selective adsorption of CO<sub>2</sub> over N<sub>2</sub>. Thus, pore surface engineering can significantly affect gas separation and storage.<sup>26</sup>

In the last few years, considerable efforts have been performed in this area. The goal of this review is to summarize the articles which have been reported recently in the field of the synthesis of COFs with the assistance of post-synthetic modifications, categorizing their different types and finally highlighting the advantages of this strategy in different applications (Fig. 1). Some reviews have been reported to classify different types of PSM methods.<sup>27–29</sup> However, attempts have been made to categorize PSM approaches based on the latest articles. Furthermore, to the best of our knowledge, for the first time we have gathered the various applications of COFs, which have been synthesized through PSM strategies. Overall, this review gives a good viewpoint to those interested in this field.

## 2. Various types of post-synthetic modifications

Post-synthetic modifications are generally divided into four main categories. The first category is post-functionalization, where diverse organic reactions occur between the present reactive groups (such as amines, carboxylic acids, hydroxyl groups, alkynes, nitro groups) and incoming components. Some of these reactions are addition-elimination reactions (amidation, esterification, and thioesterification), substitution reactions (etherification, alkylation of amines), ring-opening, click reactions, oxidation and reduction, condensation, vulcanization, and Suzuki–Miyaura-coupling reactions. Indeed in

this category covalent bonds are formed. The second category is post-metalation which is mainly based on the complexation of different metal ions such as Fe, Pd, Cu, Ir, Mn and Ru with suitable ligands, existing in the COF *via* coordination chemistry. The third category is chemical locking, also called chemical conversion in some articles. This type of modification leads to the conversion of reversible and unstable linkages into the stable linkages such as amide, quinolone, thiazole, indazole, and pyrano [4,3-*b*] pyridine. And the last category is based on host–guest supramolecular chemistry, where weak forces are responsible for post-modifications. Among these weak forces hydrogen bonding is the most usable one for the modification of COFs. Indeed, in this category, highly porous COFs act as applicable host platforms for incorporating different guest molecules. These four categories will be described in detail below.

### 2.1. Post-functionalization modifications

Three PSM strategies, amidation, esterification, and thioesterification, can be applied to compounds, bearing carboxyl groups in their backbones. The introduction of functionality *via* pre-synthetic modification of COFs may cause disturbance in the formation of COFs. On the contrary, such post-transformations are well-done with high yield, reactivity, and compatibility, and have easy workup conditions. Thus, in 2019 Yaghi *et al.* synthesized a novel COF whose carboxyl group underwent post-synthetic amidation, esterification, and thioesterification reactions, leading to the construction of absorbents for the effective elimination of some contaminants in water. The measure of the adsorption depends on the chelating properties of these anchored functionalities.<sup>30</sup> Especially amidation is substantial in biological applications. For example, Tang *et al.* used post-amidation to synthesize the new enzyme-functionalized COFs by coupling the carboxyl group in the initial COF and the amino group in glucose oxidase (GOX).

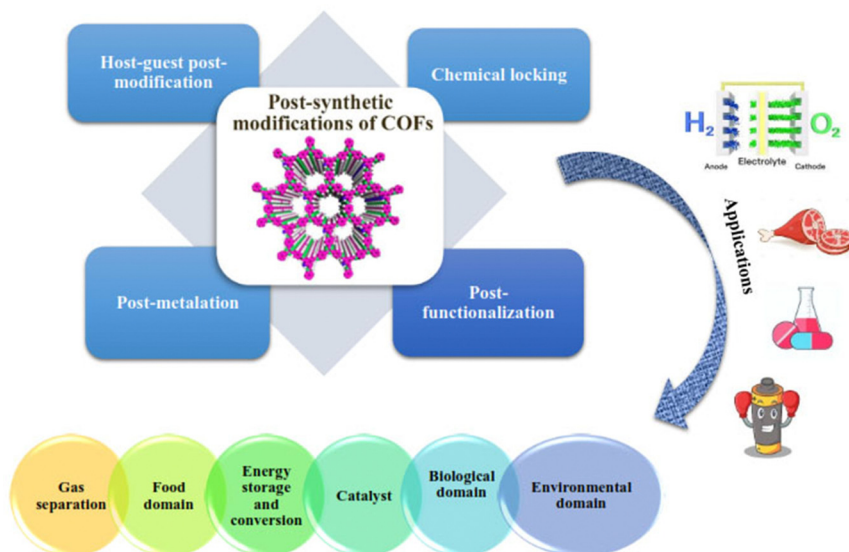


Fig. 1 Classification of different types of PSM tactics and their potential in various applications.

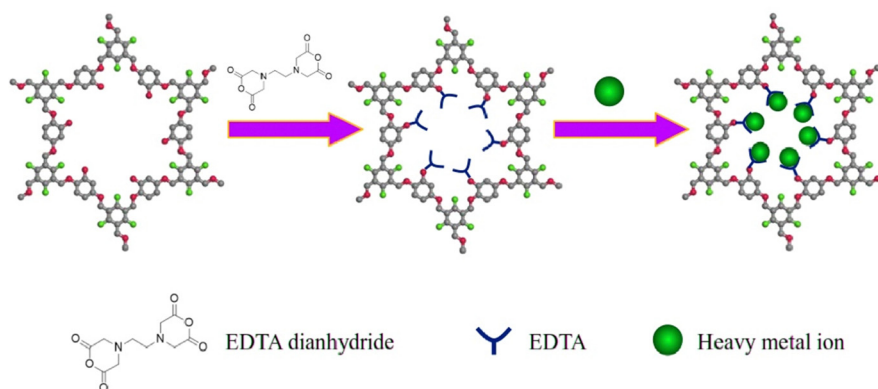


Fig. 2 Synthesis of the EDTA anchored COF for adsorption of heavy metal ions (reproduced with permission from ref. 32. Copyright 2019 American Chemical Society).

The disappearing carboxyl group peak in the solid-state  $^{13}\text{C}$ -NMR implied consuming the carboxyl functionality *via* the enzyme. Therefore, they could successfully fabricate the first COF-enzyme colorimetric biosensor for measuring the glucose concentration, in 2021. In addition, the observed similarity in the PXRD pattern proved that the post-modification did not affect crystallinity. Also, SEM and TEM indicated the similar morphologies of the parent COF, and the COF-GOX.<sup>31</sup> Furthermore, other compounds can be grafted onto COFs in the same way. EDTA is a famous chelating agent, used for the reduction of water hardness. It plays the role of a hexadentate ligand to adsorb metal ions. Grafting EDTA on COFs by the post-functionalization of the amine group in the COF with EDTA dianhydride can be easily done (Fig. 2).<sup>32</sup>

Moreover, COFs, bearing amine moieties, have been used as platforms for anchoring the desired functionalities in some other reports. For example, amino groups in frameworks can be transformed into related imine, thiourea, amide, and azo moieties by using 4-methylmercapto benzaldehyde, 4-(trifluoromethyl) phenyl isothiocyanate, 4-cyanobenzoyl chloride, and *p*-chloronitro-benzene, respectively.<sup>33</sup> Nucleophilic substitution reactions can be helpful in the post-modifications of COFs, bearing amine groups. In one effort, the amine groups in COF reacted with (1*S*)-(+)-10-camphorsulfonyl chloride to fabricate a

chiral COF with sulfonamide functionalities.<sup>34</sup> Also, nucleophilic substitution can lead to the formation of cationic COFs, an emerging category of COFs with diverse applications.<sup>35</sup> For example, this substitution reaction can be accomplished in pyridine moieties of COFs by its nucleophilic attack to bromoethane to achieve a cationic COF.<sup>36</sup>

Further types of functionalization have been reported to date. For example, with OH groups in the framework, we can fabricate carboxylic acid-functionalized COFs. This can be performed through ring opening of succinic anhydride with an OH moiety.<sup>37,38</sup> This group can also participate in the ring opening of 1,3-propane sultone to synthesize sulfoacid-based COF compounds.<sup>39</sup> In another report, hydroxyl groups at the pore walls of the COF, reacted with fluorescein-isothiocyanate (FITC). Thus, a fluorescent dye was grafted on the COF walls *via* the formation of *o*-thiocarbamate bonds. The successfully post-modified COF can be confirmed using a fluorescence microscope.<sup>40</sup> In one study, (3-aminopropyl) triethoxysilane reacted with alkyl acrylates through Michael addition to form a long chain silica precursor which can be grafted on the parent COF. In the last step, the hydroxyl groups in the initial COF participated in a sialylation reaction with prepared silane reagent through Si–O bond formation for the enhancement of hydrophobicity (Fig. 3).<sup>41</sup> In addition, a novel hydrophobic  $[\text{CF}_3]$ -COF was

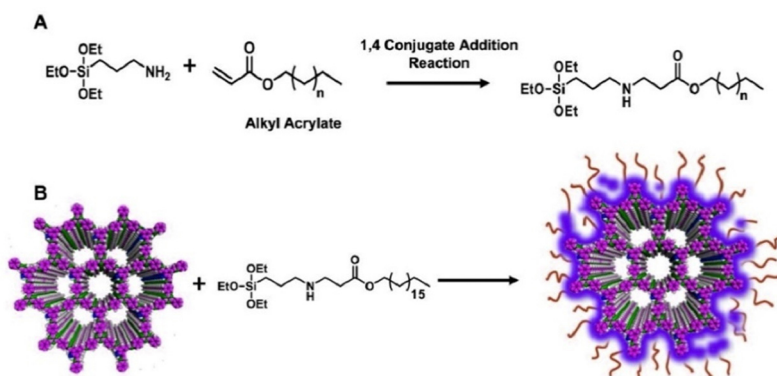


Fig. 3 (A) Synthesis of silane precursor *via* Michael addition; (B) synthesis of hydrophobic modified COF through sialylation reaction (reproduced with permission from ref. 41. Copyright 2022 John Wiley and Sons).

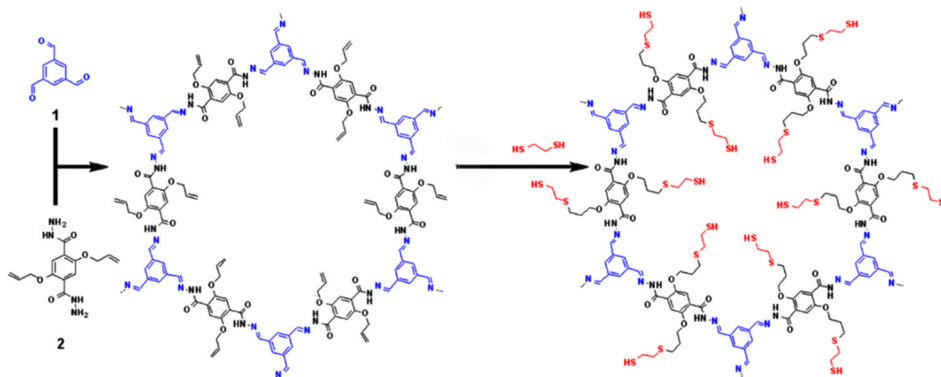


Fig. 4 Synthesis of a COF, bearing thioether and thiol arms, through the thiol-ene “click” reaction (reproduced with permission from ref. 44. Copyright 2020 Elsevier).

fabricated from [OH]-COF *via* post-silylation with dimethoxy (methyl) (3, 3, 3-trifluoropropyl) silane. Then, [CF<sub>3</sub>]-COF was loaded into the melamine sponge to form an efficient absorbent with great flame retardancy for the removal of oil from water.<sup>42</sup> Also, phenolic hydroxyl moieties can undergo post-functionalization *via* the Williamson etherification reaction. In a research study, a COF containing phenolic hydroxyl groups, reacted with (2-bromoethyl)trimethylammonium bromide, an ionic liquid, to form a cationic COF. FT-IR spectra depicted a signal at 2980 cm<sup>-1</sup>, related to anchored ammonium salt. This prepared COF has been successfully utilized as a fluorescence sensor for the detection and adsorption of ReO<sub>4</sub><sup>-</sup> contaminant from water.<sup>43</sup>

Propenyl-terminated COF can be grafted by thioether and thiol arms.<sup>44</sup> This post-modification arose from the thiol-ene “click” reaction of the COF with 1, 2-ethanedithiol to synthesize support for loading Au nanoparticles (Fig. 4). Also, the amino-modified COF was fabricated by the thiol-ene click reaction of a COF, bearing vinyl groups, with 4-aminobenzenethiol.<sup>45</sup> A carboxy-functionalized COF, an adsorbent for impressive elimination of Pb<sup>2+</sup> and Hg<sup>2+</sup> ions was fabricated *via* click reaction of a vinyl-COF with 4-mercaptobenzoic acid.<sup>46</sup> In another report, an alkynyl-functionalized COF was applied for the synthesis of a phenylboronic acid-decorated COF *via* the azide-alkyne “click” reaction with azide-phenylboronic acid. This novel composite was used for the enrichment of glycopeptides.<sup>47</sup> 3D COFs have been less studied compared to 2D COFs due to some difficulties in their synthesis. These problems will be intensified for the synthesis of 3D functionalized COFs from precursors with desirable functional groups. The reason is attributed to the spatial effects. PSM is a reasonable method for constructing 3D functionalized COFs by introducing functionalities into a predetermined platform. In 2022, Wang *et al.* developed a series of novel highly crystalline 3D COFs through post-synthetic azide-alkyne cycloaddition with copper catalyst. Using various azide compounds caused the grafting of different functionalities on the pore walls for evaluating the selectivity toward CO<sub>2</sub>/NO<sub>2</sub> gases.<sup>48</sup> Furthermore, vinyl groups in COFs can be converted to quinazolinone *via* a photocatalytic reductive cyclization reaction

between them and a 2-aminobenzamide reagent. The produced quinazolinone-anchored COF benefits from high nitrogen content and an extended  $\pi$ -conjugated system, leading to suitable adsorption of I<sub>2</sub>.<sup>49</sup>

The Suzuki-Miyaura-coupling reaction, a well-known strategy for carbon-carbon bond formation, can be employed to modify COFs. A novel chiral COF was designed *via* the Suzuki-Miyaura reaction between a COF, bearing Br groups, and 4-borono-L-phenylalanine in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (Fig. 5)<sup>50</sup>. Furthermore, this coupling reaction has been exploited for introducing a variety of functionalities such as formyl, cyan, trifluoromethyl, methylthio, and carbomethoxy to a brominated COF by its reaction with phenylboronic acids, bearing the corresponding functionalities. Also, Pd(PPh<sub>3</sub>)<sub>4</sub> is present in the reaction media as a catalyst.<sup>51</sup>

Moreover, carbonyl moieties of COFs can participate in a post-functionalization strategy. For example, vulcanization is an interesting strategy for the post-transformation of C=O bonds in polyimide COFs to C=S bonds through the Lawesson reagent. This formed COF exhibited improved electrochemical performance<sup>52</sup>. In another effort, a cyclocondensation post-modification strategy was applied to achieve two extended  $\pi$ -conjugated COFs. Indeed a boronic ester-based COF, containing pyrene-4, 5-dione building blocks, underwent a condensation reaction with *o*-phenylenediamine and 2,3-diaminonaphthalene to form pyrene-fused pyrazaacene COFs (Fig. 6). Pyrazaacene moieties consist of a pyrazine ring along with fused aromatic rings which offer superior electronic properties.<sup>53</sup>

A post-synthetic oxidation strategy with *m*-CPBA was developed for tuning the optoelectronic features of the fully conjugated thiophene-containing COF, used as a photocatalyst. Indeed the introduction of sulfone groups through the oxidation of thiophene moieties was responsible for its optoelectronic properties.<sup>54</sup> As post-synthetic oxidation, post-synthetic reduction can also be a helpful post-treatment strategy. For example, the first two-step post-modification of COFs was reported in 2016, whose first step was reducing the nitro groups in the pores to amine groups by tin(II) chloride dihydrate, and the second step was aminolysis of acetic anhydride to produce

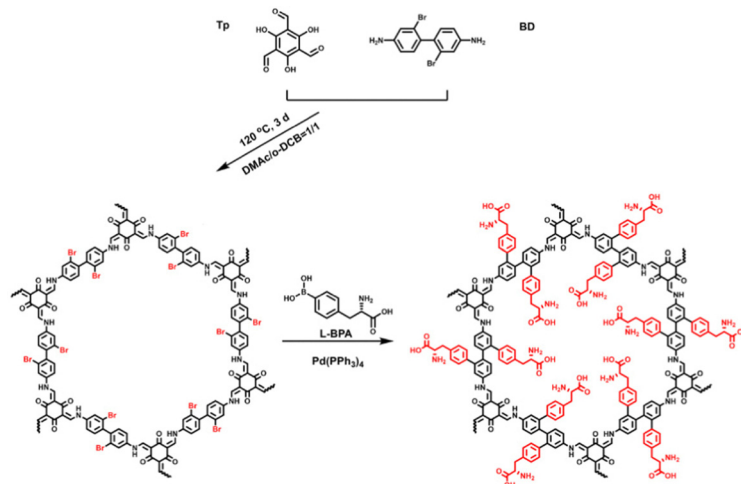


Fig. 5 Synthesis of novel chiral L-phenylalanine decorated COF (reproduced with permission from ref. 50. Copyright 2023 The Royal society of chemistry).

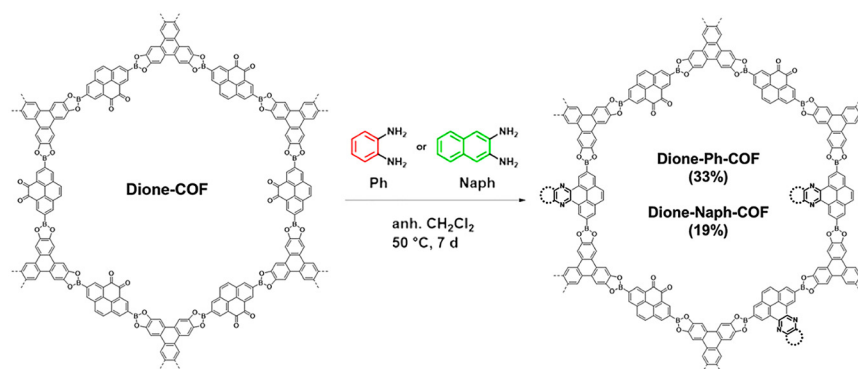


Fig. 6 Cyclocondensation post-modification strategy for pyrene-fused pyrazaecene COF preparation (reproduced with permission from ref. 53. Copyright 2022 Elsevier).

amide moieties. According to H-bonding interactions, this functionalized COF was employed for the adsorption of lactic acid which is a precursor in biodegradable plastic formation.<sup>55</sup> Using NO<sub>2</sub> groups as masking forms of NH<sub>2</sub> groups has been exploited in some other reports to introduce amine groups in the platform. For example, in one study, two functionalized COFs, COF-NO<sub>2</sub> and COF-NH<sub>2</sub> were prepared. The COF-NO<sub>2</sub> was synthesized from the parent COF by the Povarov reaction, but COF-NH<sub>2</sub> was produced by adding on one more post-treatment step, the reduction of COF-NO<sub>2</sub> with stannous chloride instead of using the Povarov reaction directly (Fig. 7). The parent COF is produced by the Schiff-base reaction, which is a reversible condensation reaction. Thus, amino functionalities in monomers can react with aldehyde groups, formed from the breaking of C=N bonds, during the Povarov reaction. That's why COF-NH<sub>2</sub> was synthesized indirectly.<sup>56</sup>

Radical reactions can also participate in the post-modification of COFs. For instance, Yan *et al.* in 2017, introduced quaternary-ammonium-functionalities to a COF to

obtain an anion exchange membrane for fuel cell applications. For this aim, biphenyl moieties of the parent COF, containing methyl substituents, reacted with N-bromosuccinimide (NBS) for bromination of benzylic methyl groups through a radical reaction, and then, quaternization was fulfilled through the reaction between brominated COF and trimethylamine. Finally, its counteranion (Br<sup>-</sup>) was replaced with OH<sup>-</sup> by treating it with KOH.<sup>57</sup>

## 2.2. Post-metalation

In contrast to post-functionalization with covalent bond formation, metallic COFs can be achieved by post-synthetic modifications through the coordination of metals to ligand-containing COFs. These are used as catalysts, Li-ion battery electrolytes, gas adsorbents, and sensors with practical applications. For example, an imine-based COF, containing catechol sites, is fabricated to chelate Fe<sup>3+</sup> to form an efficient catalyst for ring-opening of epoxides with alcohols.<sup>58</sup> In another report, for electrochemical sensing applications, an iron-porphyrin-

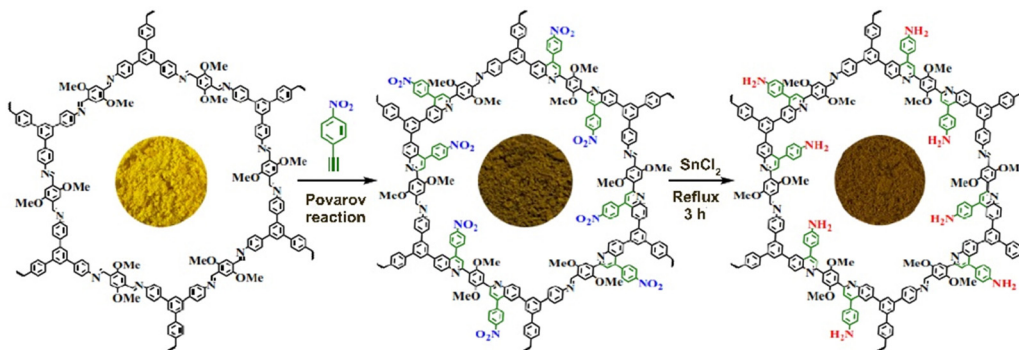


Fig. 7 Synthesis of COF-NH<sub>2</sub> and COF-NO<sub>2</sub> (reproduced with permission from ref. 56. Copyright 2021 Elsevier).

based COF was fabricated *via* the post-metalation of a porphyrin-based COF with FeCl<sub>2</sub>·4H<sub>2</sub>O. Indeed nitrogen atoms in the porphyrin ring provide coordination sites for Fe<sup>2+</sup>.<sup>59</sup> In addition to iron other metals have been successfully chelated to binding sites of COFs. For instance, a 2D porphyrin-based COF was fabricated and then, post-metalized by Co and Cu, which showed admirable room-temperature sensing performance toward gases. In particular, the Co-COF one demonstrated a rarely reported high selectivity toward NO<sub>2</sub> with a LOD of 6.8 ppb.<sup>60</sup> Also, in another effort, three COFs containing suitable binding sites, were prepared for grafting Pd<sup>2+</sup>. These frameworks were constructed *via* the addition of 2,6-diformylpyridine, 2,6-diformylbenzene, and 4-*tert*-butyl-2,6-diformylphenol starting monomers to 2,4,6-4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline to form three scaffolds with N-, N-N- and N-O-binding sites respectively. Finally, these COFs were treated with Pd(OAc)<sub>2</sub> in tetrahydrofuran to synthesize metal-anchored COF-based heterogeneous catalysts.<sup>61</sup> In addition, *N,N'*-bis(salicylidene)ethylenediamine (salen) is an important ligand for coordinating and stabilizing metal ions. In one study, a salen-based COF was post-metalized with different metal acetates as shown in Fig. 8.<sup>62</sup> Also, phthalocyanine is another convenient ligand for chelating metals to form metallophthalocyanine COFs.<sup>63</sup> Moreover, in one research study, two chiral diphosphine-based COFs were produced and subsequently underwent post-metalation with Ir and Ru elements. Indeed, phosphine ligands coordinate with these transition metals to form efficient catalysts for enantioselective hydrogenation. Successful post-metalation confirmed by solid-state <sup>31</sup>P NMR. These porous catalysts can adsorb and concentrate hydrogen. Therefore, hydrogenation can be accomplished under ambient pressure.<sup>64</sup> Also, Ni can be anchored to COFs *via* post-synthetic metalation. For the first time in 2016, McGrier and coworkers provided a three-dimensional boronic acid-based COF with conjugated dehydrobenzoannulene units for Ni binding through the strong  $\pi$ -metal complex formation with Ni. This COF demonstrated a good adsorption capacity toward ethane and ethylene.<sup>65</sup>

Furthermore, ionic interactions can also participate in the formation of metallic COFs.<sup>39</sup> For instance, in one effort, an ionic COF was prepared *via* the treatment of an -N-H

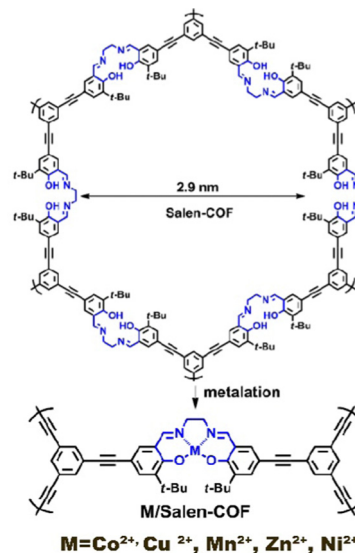


Fig. 8 Post-metalation of salen-based COFs. Synthesis of the EDTA anchored COF for adsorption of heavy metal ions (reproduced with permission from ref. 62. Copyright 2017 American Chemical Society).

containing COF with LiH (or NaH). After this post-metalation -N-Li<sup>+</sup> (or -N-Na<sup>+</sup>) sites were formed in the framework, which was confirmed by X-ray photoelectron spectroscopy (XPS).<sup>66</sup> Also, in one study, an imidazole based-COF was post-metalized with *n*-BuLi to achieve considerable lithium ion conductivity (more than  $7.2 \times 10^{-3}$  S cm<sup>-1</sup>) for using as the Li-ion battery solid-state electrolyte.<sup>67</sup>

### 2.3. Post-synthetic locking

Crystalline COFs have been obtained through reversible reactions which are crucial for defect healing or disorder correction. In other words, these reactions are thermodynamically controllable. Nevertheless, reversibility can have a negative effect on COF stability. Thus, the chemical conversion of reversible COFs into irreversible ones, called post-synthetic locking, leads to an improvement in chemical stability. This strategy was developed by Yaghi *et al.*, to form an amide-linked COF from the initial imine-linked framework.<sup>68</sup> Also, in one report, published in

2023, imine-linked COFs were successfully converted to bis-amide compounds *via* post-synthetic Ugi reaction. Indeed the Ugi reaction is a multicomponent reaction among imine, isocyanide, and carboxylic acid reagents to produce a bis-amide adduct.<sup>69</sup> In another effort, an unstable imine linkage in the ortho position of hydroxyl groups was transformed into a heteroaromatic benzoxazole linkage through post-oxidative cyclization with DDQ.<sup>70</sup> Also, an imine linkage can be successfully converted into a rigid thiazole linkage by post-synthetic modification with the sulfur element. At first, imine was oxidized to a thioamide by sulfur element and then, this intermediate was converted to a thiazole ring by cyclization.<sup>71</sup> Furthermore, aza-Diels–Alder cycloaddition reaction, occurring between arylalkynes and aryl imines is a reasonable strategy for post-locking. In one study, (4-ethynylphenyl) boronic acid underwent aza-Diels–Alder cycloaddition with an imine-linked COF to introduce boronic acid ligands into the COF *via* post-modification strategies. Due to the generation of stable five and six-membered cyclic esters between boric acid moieties and *cis*-diol compounds, this novel locked COF is capable of capturing *cis*-diol materials. It is worth noting that the fluorescent properties of quinolone linkage, formed from cycloaddition, can be helpful for identifying *cis*-diol substances.<sup>72</sup> In addition, an extremely conjugated 3D COF, bearing pyrazine, triazine, and quinolone moieties, was synthesized *via* a post-treatment strategy. The imine linkages in the initial COF underwent the Povarov reaction with styrene to form a quinolone-linked COF (Fig. 9). The obtained fully  $\pi$ -conjugated and nitrogen-rich COF depicted excellent stability and ionic conductivities which made it suitable for lithium-ion batteries electrodes.<sup>73</sup> The Doebner reaction is another helpful strategy for the chemical conversion of reversible imine-linked COFs to stable quinolone-linked COFs. Indeed, it is a three-component reaction between aldehyde, amine, and pyruvic acid reagents to form quinoline-4-carboxylic acids. This reaction can be exerted either in a one-pot or a post-synthetic modification method. The initial imine-linked COF, constructed *via* a condensation reaction between the related aldehyde and amine, can be attacked by an enolic form of pyruvic acid subsequently. Finally, electrophilic

addition and rearomatization result in forming the stable 4-carboxyl-quinoline linked COF.<sup>74</sup> Furthermore, the cadogan reaction can be employed to form irreversible indazole and benzimidazolylidene linkages from imine linkages through the reductive cyclization of *o*-nitroaryl imine compounds with a phosphine reagent (Fig. 10).<sup>75</sup> Also, there are some other reports on chemical conversion of imine linkages into irreversible ones. For instance, in one work hydrazone linkages have been converted to hydrazide linkages *via* oxidation with sodium chlorite. The hydrazide-linked COF showed excellent stability under harsh conditions. In addition, due to the appropriate interactions between hydrazide moieties and I<sub>2</sub> molecules, the oxidized framework depicted remarkable iodine uptake compared to the hydrazone-linked COF.<sup>76</sup> Some more complex reactions can be exploited for these transformations. For example, in one study, a cascade sequence was proposed to obtain pyrano[4,3-*b*]pyridine-linked COF derivatives. As illustrated in Fig. 11, this one-pot cascade protocol includes Schiff-base condensation, [4+2] cycloaddition reaction, and finally dehydroaromatization.<sup>77</sup>

However, most of the time, there is more than one post-modification that can be performed in one step<sup>78</sup> or multi-steps. For instance, a 2D COF has been synthesized by post-modification through three steps: the first step is the reduction of imine linkages to the related amine. Then, sulfonic acid groups are anchored on COF by the reaction of the amine with 1,3-propane sultone, and the last step is a metathetical reaction of cobalt acetate with alkyl sulfonic acid. These reactions are a combination of post-locking, functionalization, and metalation respectively.<sup>79</sup>

#### 2.4. Host-guest post-modification

In addition to the three categories mentioned earlier, there are other types of post-functionalization that have been comparatively less researched. Owing to the highly porous structures of COFs, they are perfect host platforms for embedding guest molecules like C<sub>60</sub> molecules<sup>80</sup> through host-guest supramolecular chemistry. In contrast to post-functionalization with covalent bond formation, weak forces including van der Waals,

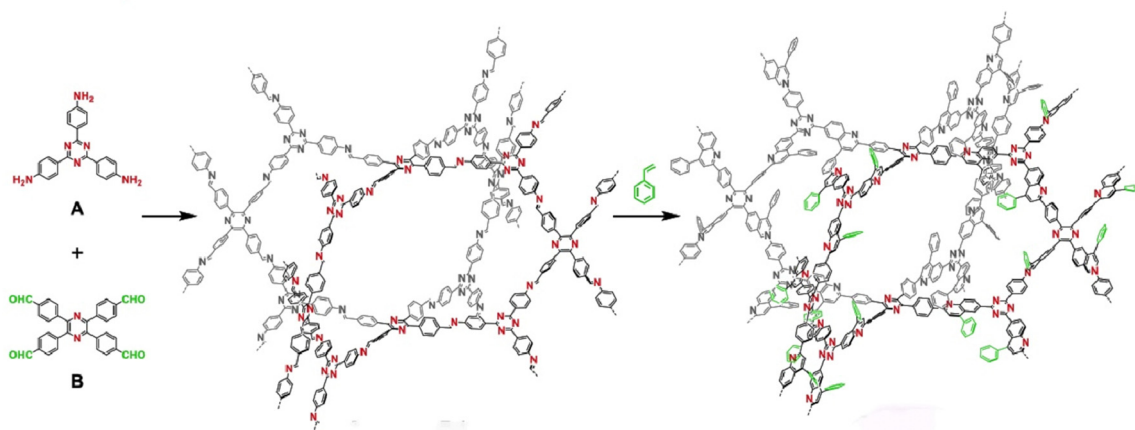


Fig. 9 Synthesis of 3D highly conjugated COF (reproduced with permission from ref. 73. Copyright 2022 American Chemical Society).

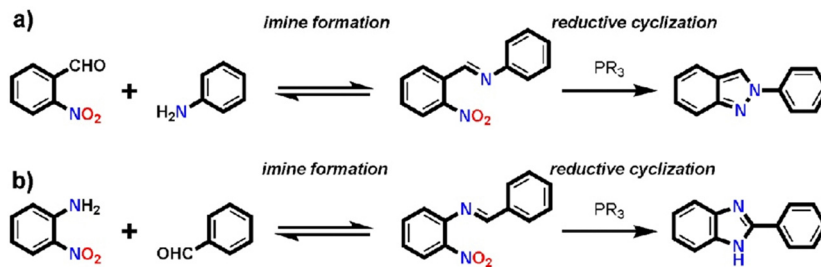


Fig. 10 Cadogan reaction used for imine-linkage conversion (reproduced with permission from ref. 75. Copyright 2022 American Chemical Society).

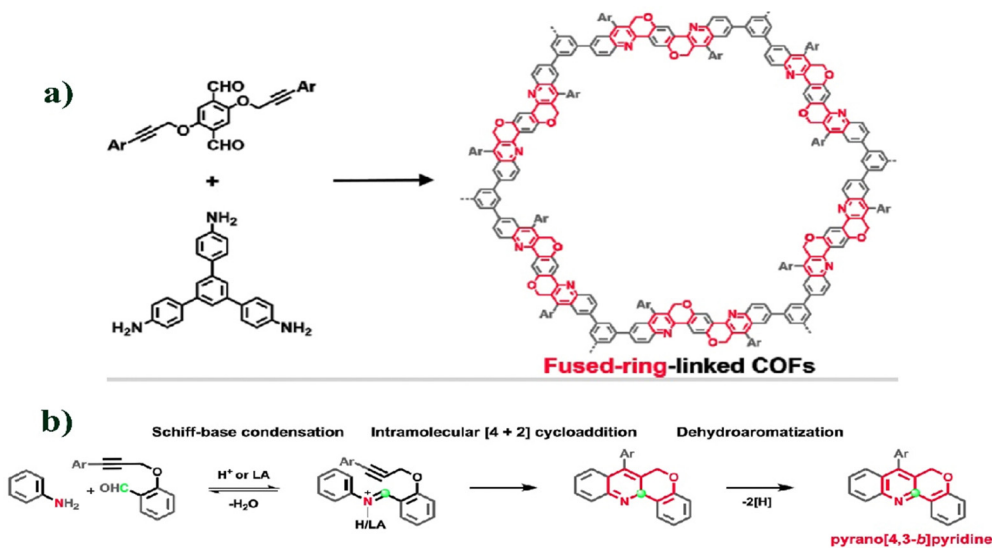


Fig. 11 (a) The prepared rigid-linked COF. (b) COF cascade sequence for pyrano[4,3-*b*]pyridine linkage formation (reproduced with permission from ref. 77. Copyright 2022 American Chemical Society).

hydrogen bonding, and  $\pi$ - $\pi$  interactions are responsible for this modification. For example, in one research, photoresponsive metal-organic polyhedra (PMOP) particles, which were prepared *via* the coordination of  $Cu^{2+}$  to 5-((2,4-dimethylphenyl) diazanyl)

isophthalic acid ligands, were introduced to a COF to construct a photoresponsive adsorbent for propylene. PMOP motifs were dispersed into the COF pores *via* impregnation. The azobenzene moieties of PMOP had *trans* configuration under visible-light

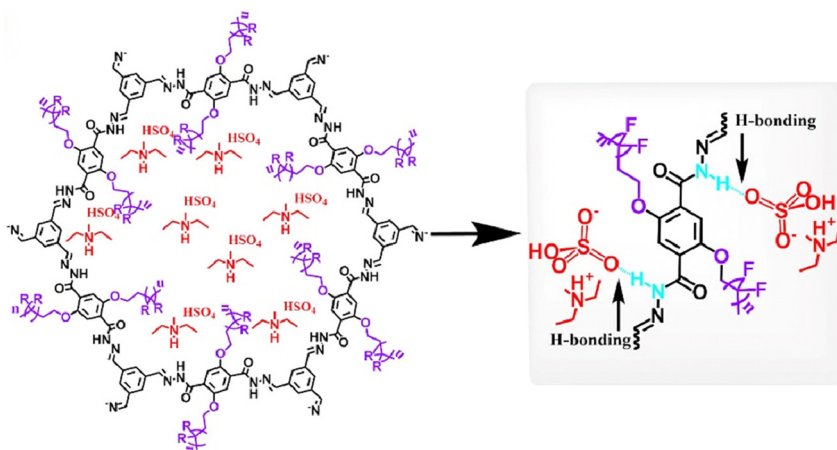


Fig. 12 Hydrogen bond networks in the protic ionic liquid doped COF (reproduced with permission from ref. 82. Copyright 2021 American Chemical Society).



irradiation, leading to  $C_3H_6$  adsorption but under UV-light irradiation, configuration transformation occurred, and *cis* conformation was achieved which led to propylene desorption.<sup>81</sup> In another work, protic ionic liquids, as proton carriers, were doped into the pores of COFs *via* hydrogen bond formation between ionic liquids and COFs to promote proton conductivity (Fig. 12).<sup>82</sup> Further guest molecules like trimesic acid have been accommodated in COF-based materials through host-guest chemistry. Indeed hydrogen bond formation between carboxylic acid groups of trimesic acid and carbonyl groups of COF caused trimesic acid's selective adsorption to special sites in the pores of the framework.<sup>83</sup>

### 3. Various applications of post-modified COFs

Due to the recent drastic increase in published papers in the field of COF synthesis through post-treatment strategy, a number of reviews have been written about different post-modified COFs with particular applications.<sup>84–88</sup> Different interactions between these functionalities and other molecules (such as biological molecules, pollutants, ions) are responsible for the binding of these molecules to COFs in various applications such as adsorbents and sensors. Also, these functionalities can affect the pore size of the COFs which leads to the strengthening of these bindings. In this part, various applications of post-modified COFs which have been reported to date are briefly summarized.

#### 3.1. Environmental applications

**3.1.1. Greenhouse gas capture.** Global concerns regarding the growth of  $CO_2$  in the atmosphere, which leads to climate change, are increasing. Thus, to solve this environmental issue, considerable efforts have been implemented. For example, introducing ionic liquids or carboxylic acid functionalities to COFs *via* the reaction of their phenolic hydroxyl groups with (2-bromoethyl)triethylammonium bromide or succinic anhydride respectively, can improve the  $CO_2$  uptake potential of these frameworks. This significant adsorption is ascribed to decreasing the size of pore walls, and the affinity of anchored functionalities toward quadrupole  $CO_2$  molecules.<sup>89,90</sup> Also,  $SF_6$  is another greenhouse gas whose warming potential is much more than  $CO_2$ . The formerly mentioned trifluoromethyl functionalized COF was applied as a suitable adsorbent for this gas. Indeed  $-CF_3$  groups caused reduction in the COF pore size to boost the binding strength with  $SF_6$  molecules.<sup>51</sup> Furthermore, in one report, two 2D and 3D cobalt-metalated COFs were synthesized *via* post-modification to produce suitable chemosensors for CO gas detection.<sup>91</sup>

**3.2.2. Radioactive element uptake.** Another environmental issue is the detection and adsorption of uranium, consumed by the nuclear industry for the production of nuclear energy. This element is radioactive and toxic. Thus, widespread efforts have been performed for the efficient removal of uranium from the environment. An amidoxime functionalized COF with high

adsorption capacity ( $436\text{ mg g}^{-1}$ ) is a good candidate to achieve this aim. The parent COF was formed *via* the Knoevenagel condensation between 2,4,6-tris(4-formylphenyl)-1,3,5-triazine and 2,2'-(1,4-phenylene)diacetonitrile. Thus, the  $sp^2$  carbon conjugated COF depicted excellent fluorescence properties. Furthermore, amidoxime groups are binding sites for the rapid capture of  $UO_2^{2+}$  (Fig. 13), resulting in quick fluorescence quenching. Also, its detection limit is reported to be 8.3 nM, less than the maximum standard determined by the U.S. Environmental Protection Agency (130 nM).<sup>92</sup> Radioiodine, existing in nuclear waste, is another harmful substance. The cationic COF, whose synthesis method was expressed earlier, was employed for efficient iodine uptake. Indeed the electrostatic interactions between cationic COF and iodine molecules are responsible for this improved iodine adsorption capacity.<sup>36</sup> Also, in one study a hydrazone-linked COF was converted to a hydrazine-linked COF under reduction conditions with  $NaBH_4$ . The presence of abundant NH groups in the framework which can lead to the formation of hydrogen bonds with radioactive iodine molecules, made this hydrazine-linked COF an excellent platform for iodine uptake from both gas and solution phases.<sup>93</sup>

**3.3.3. Water remediation.** Carboxylic acid pesticides, utilized for improving agricultural crop yield, are an environmental threat. Some of them are teratogenic and carcinogenic and due to their good solubility arising from high polarity, they can quickly enter the surface water. The World Health Organization, U.S. Environmental Protection Agency, and European Union have determined the maximum permissible value of each pesticide in drinking water. As previously mentioned, an amino-modified COF, used as a solid phase extraction absorbent, was synthesized through the thiol-ene click reaction. Amino groups in COF make it possible to interact with the anionic carboxylate headgroup of pesticides, leading to efficient extraction of them from water samples.<sup>45</sup> Furthermore, some other kinds of contaminants such as heavy metals exist in water, and their removal has gained significant importance. Exposure to mercury ions, a bioaccumulative and toxic element, can severely damage the eye, muscle, and skin. Therefore, in one effort, two thiol-functionalized COFs were designed by thiol-ene click reaction of a vinyl-containing COF with bis (2-mercaptoethyl) sulfide and dithiothreitol. XPS and elemental analysis data confirmed the successful post-functionalization of COF. Thioether and thioalcohol groups are suitable binding sites for the removal of  $Hg(II)$  from water and the adsorption capacities of these prepared COFs were reported to reach 586.3 and 535.5  $mg\text{ g}^{-1}$ , respectively.<sup>94</sup> Also, a COF-based electrochemical sensor for the detection of  $Cu(II)$  in seawater was designed in three steps including synthesis, introducing sulfhydryl functionality to carbon nanotube-doped COF *via* thiol-ene click reaction, and electrochemical deposition of Au nanoflower to the formed nanocomposite. The promoted conductivity of this electrochemical sensor was confirmed by cyclic voltammetry (CV).<sup>95</sup> Another class of water contaminants is non-steroidal anti-inflammatory drugs (NSAIDs). NSAIDs are commonly prescribed for pain relief and inflammatory control.

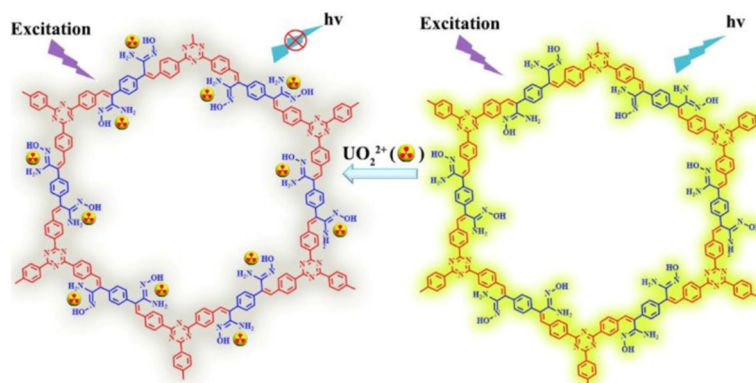


Fig. 13 Application of the amidoxime functionalized COF in the  $\text{UO}_2^{2+}$  adsorption (reproduced with permission from ref. 92. Copyright 2020 The Royal society of chemistry).

However, wastewater, containing the remaining NSAIDs, has been considered as aquatic life-threatening. So, removing them with adsorbent materials is an interesting domain for researchers. The two previously mentioned COFs (Fig. 7) were employed for evaluating the adsorption selectivity toward NSAIDs. Ketoprofen, ibuprofen, and naproxen were considered model molecules. Due to hydrogen bond formation between carboxylic acid and carbonyl groups in these model molecules and the amino groups in  $\text{COF-NH}_2$ , it showed good selectivity toward three NSAIDs compounds, especially ketoprofen. However, this selectivity wasn't seen in COF with the nitro group.<sup>56</sup> In another work, diclofenac sodium, a commonly used NSAID, was successfully removed from wastewater by amine-grafted COFs. These functionalized COFs were obtained *via* a thiol-ene click reaction between a vinyl-COF and thiol compounds, bearing amino groups. For pore size tuning, the chain length of thiol agents was changed in three COFs. The COF with a chain of three carbon atoms showed unprecedented adsorption capacity toward diclofenac. In addition to suitable pore size, this result is attributed to electrostatic, hydrogen bonding, hydrophobic and  $\pi$ - $\pi$  interactions as illustrated in Fig. 14.<sup>96</sup> The next water contaminant is oil, entering the water through industrial processes. Using superhydrophobic materials is helpful for the efficient extraction of oil from water. For this aim, an imine-based COF, containing hydroxyl groups, was reacted with ( $\pm$ )-glycidol to form vicinal diols *via* the ring-opening process. In the next step, diols underwent a reaction with perfluorooctyltriethoxysilane to produce a stainless-steel net-supported superhydrophobic coating for oil/water separation with an efficiency over 99.5% and a water contact angle of  $152.1^\circ$ . Indeed, the initial imine-based COF was prepared on the support before post-synthetic modifications. Also, it has been claimed that until 50 separation cycles, the efficiency didn't fall below 99.5%.<sup>97</sup> In another work, a non-fluorinated superhydrophobic COF (Fig. 3) was utilized for effective oil/water separation from its emulsion.<sup>41</sup> Organic dyes are hazardous water pollutants like the already mentioned contaminants. For their efficient removal, in one attempt, a carboxyl-containing COF was prepared as the initial adsorbent platform. In the next step,

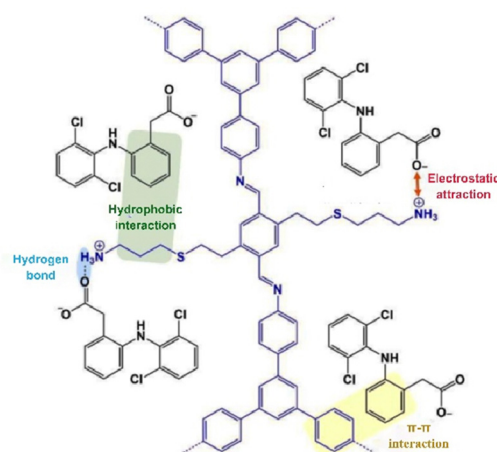


Fig. 14 Different interactions between functionalized COF and diclofenac (reproduced with permission from ref. 96. Copyright 2023 Elsevier).

it was post-metalized *via*  $\text{Ca}^{2+}$  and  $\text{Ni}^{2+}$ . Although the carboxyl-containing COF due to hydrogen bonding and  $\pi$ - $\pi$  stacking interactions showed reasonable adsorption ability toward Congo red dye, the post-modified ones exhibited better performance. The reason for this is attributed to the additional electrostatic interactions. The reported adsorption capacity for  $\text{Ca}^{2+}$  and  $\text{Ni}^{2+}$  decorated platforms are  $704.23 \text{ mg g}^{-1}$  and  $781.25 \text{ mg g}^{-1}$ , respectively.<sup>98</sup> Organoarsenic compounds such as roxarsone (4-hydroxy-3-nitrophenyl arsonic acid) are employed in the poultry industry as feed additives. Nevertheless, due to their toxicity, their detection in and adsorption from wastewater, have attracted researchers' attention. For this aim, two amidoxime-functionalized COFs were prepared through post-synthetic modification of existing cyano groups with hydroxylamine. A disappearing  $-\text{CN}$  stretching band in FT-IR confirmed post modification was performed successfully. Strong hydrogen bonds between these functionalized COFs and the  $-\text{AsO}(\text{OH})_2$  moiety of roxarsone make the prepared COFs promising adsorbents for roxarsone removal from wastewater. Furthermore, due to the  $\pi$ -conjugated structures of these two

COFs, they are utilized as efficient fluorescence sensors for roxarsone detection simultaneously.<sup>99</sup> Oxoanions including  $\text{ReO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , and radioactive  $^{99}\text{TcO}_4^-$  are the other toxic water pollutants. Neutral COF resins can be converted to cationic COFs as ion-exchange sorbents for efficient oxoanion scavenging. In one report, 2,4,6-collidine participated in a Knoevenagel reaction with benzaldehyde through melt polymerization conditions and in the next step was post-functionalized with hydrochloric acid to form the desired ionic COF. This cationic olefin-linked COF resin showed an admirable ion-exchange ability and adsorption capacity of more than  $1087 \text{ mg g}^{-1}$  for  $\text{ReO}_4^-$ .<sup>100</sup>

### 3.2. Biological applications

**3.2.1. Drug delivery.** Creating agents which can recognize tumor cells from healthy tissues is very essential for safe cancer therapy. In one study, a biocompatible folate-functionalized COF nanocomposite was fabricated for drug delivery to kill cancer cells. It was synthesized *via* a condensation reaction between aldehyde groups in the parent COF and folic acid amino groups. The post-modified framework was loaded with Withaferin A, an anticancer drug. As expected for efficient cancer-targeting, this platform not only exhibited excellent affinity toward FR-positive cancer cells but also demonstrated no remarkable damage in the healthy organs of mice. Also, due to its sufficient pore size, folate-decorated COF showed an acceptable capacity for drug loading.<sup>101</sup>

**3.2.2. Biosensors.** Hydrazine is applied as a precursor for fabricating diverse chemical materials, including polymers, antioxidants, and pharmaceuticals. It can be either absorbed through the skin, digestive and respiratory tracts or even formed during the metabolism of some drugs like isoniazid. The liver, central nervous system, lungs, and some other parts of our body are susceptible to being hurt by hydrazine. So, the development of fluorescent sensors for detecting hydrazine, existing in our body, is interesting but immature.<sup>102</sup> For this aim, an imine-based COF was formed initially. Then, to gain better fluorescence quantum yield, the parent COF was post-modified through the reaction between its hydroxyl groups and acetic anhydride. Fluorescence spectrum data confirmed that this COF is a promising sensor for detecting hydrazine, formed in mouse liver cells during isoniazid metabolism.<sup>103</sup> Also, constructing COF-based sensors is of particular importance to detect and control other threats to human health. Diabetes mellitus is a glucose metabolic deficiency and usually, patients suffer hyperglycemia which can damage their different organs. As noted earlier a glucose oxidase enzyme functionalized COF was synthesized as a colorimetric biosensor for quantitative concentration determination of the glucose in serum and urine samples. Due to the sensitivity of most enzymes to operating conditions and demanding mild temperature and pH, immobilization of the enzyme on the COF platform *via* the post-modification method is suitable for designing a biosensor, exploited in medical diagnostics.<sup>31</sup> Moreover, among the third generation of fluoroquinolone-based antibiotics, norfloxacin with a wide range of antibacterial activities was a commonly

used drug. However, due to some perilous side effects, its prescription has become limited. Also, the sensitive detection of its remaining values arising from defective metabolism is of great interest. For this purpose, a  $\beta$ -cyclodextrin porous polymer with considerable surface area was functionalized to a COF and then,  $\text{Pd}^{2+}$  was doped into this nanocomposite to construct an electrochemical sensor for norfloxacin detection.<sup>104</sup>

**3.2.3. Biomarker capture.** Exosomes are small vesicles that can transmit different biomolecules such as nucleic acids, proteins, and lipids. After release from either healthy or diseased cells, exosomes can be found in all body fluids, including blood, saliva, and urine. Exosomes are used as disease biomarkers for cancer, immunodeficiency, and Alzheimer's disease. Therefore, the separation of exosomes from human serum is an interesting method for disease diagnosis. In one report, a hydrophilic COF was synthesized *via* a post-synthesis modification strategy for exosome adsorption. For this aim, an imine-based COF was fabricated by condensation reaction and then, vinyl functional groups in the COF underwent click reaction with 1,2-ethanedithiol leading to grafting Au NPs through the S–Au bond formation. In the last step, glutathione and cysteine were immobilized onto Au NPs to increase hydrophilicity for exosome capturing, which is verified by TEM images.<sup>105</sup>

**3.2.4. Chiral column chromatography.** Chirality is a vital attribute of biological systems. In most racemic drugs only one conformation is medicinally active while the other conformation can even be toxic. So, separation techniques such as chromatography with chiral stationary phases for gaining enantiopure drugs are remarkable. Chiral COFs such as  $\beta$ -cyclodextrin covalent organic frameworks ( $\beta$ -CD COFs), used as stationary phases, are good candidates for effective enantio-separation. Due to hydroxyl and amino groups presented in  $\beta$ -cyclodextrin derivatives, the desired functionalities can be introduced into these COFs. In one report, two functionalized  $\beta$ -CD COFs were prepared for selective enantio-separation of dihydropyridines and fluoroquinolones. In these post-modifications, the parent  $\beta$ -CD COF reacted with 1,4-butane sultone and (+)-diacetyl-L-tartaric anhydride. Molecular docking simulation data revealed these functionalities enable more interactions between chiral selectors in the COF skeleton and enantiomers. Also, due to the dual-chiral platform, the tailored COF with (+)-diacetyl-L-tartaric anhydride depicted efficient selectivity for acidic chiral drugs.<sup>106</sup> Other functionalized COFs have been investigated for using as chromatographic stationary phases. For example, the previously mentioned chiral COF (Fig. 5) can be a good candidate for the selective separation of racemic phenylalanine.<sup>50</sup> Also, in another research,  $\text{SOCl}_2$  was added to [(1-phenylethyl) amino] acetic acid to form the related acyl chloride which was utilized as an esterifying agent. A COF, containing hydroxyl groups, underwent an esterification reaction with the prepared acyl chloride. This functionalized COF was employed as the stationary phase of the gas chromatographic capillary column for isomer separation. The grafted benzene ring, amine, and carbonyl moieties boosted  $\pi$ – $\pi$ , and hydrogen-bonding interactions, which led to enhanced isomer resolution.<sup>107</sup>

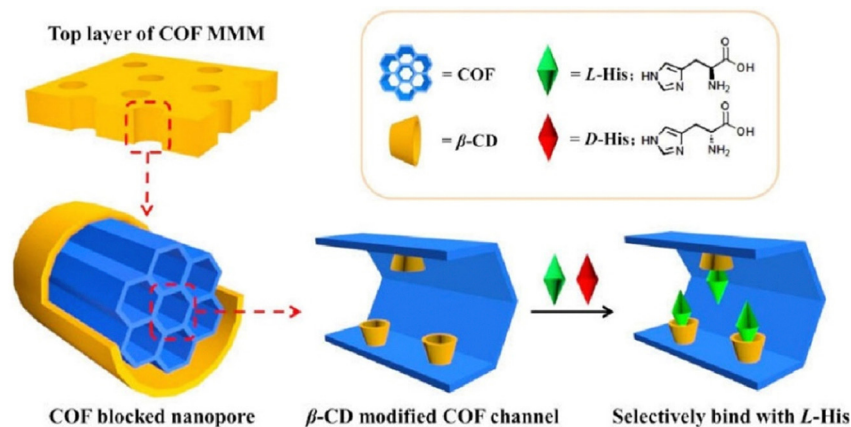


Fig. 15 Function principles of the  $\beta$ -cyclodextrin grafted COF in a MMM system (reproduced with permission from ref. 108. Copyright 2019 American Chemical Society).

**3.2.5. Solid-state smart nanochannels.** Imitating the cellular transmembrane transport mechanism is of interest to develop artificial solid-state nanochannels for enantioselective transportation of amino acids. For the first time in 2019, a 2D COF was reported as a filler to produce a mixed matrix membrane (MMM) that is capable of transmembrane transportation of *L*-histidine. COFs with functionalizable nanochannels are promising candidates for transporting ions and molecules. Indeed, the 2D COF was obtained *via* post-functionalization of the initial COF with chiral  $\beta$ -cyclodextrin through a thiol-ene click reaction. The suggested mechanism for selective adsorption of *L*-His is as follows: the hydrophobic imidazole ring of the histidine is placed into the hydrophobic cavity of the COF and polar moieties of histidine such as carboxyl and amino groups are outside of the COF cavity and interact with  $\beta$ -cyclodextrin hydroxyl groups (Fig. 15).<sup>108</sup>

### 3.3. Energy storage and conversion applications

**3.3.1. Lithium-sulfur batteries.** Due to growing demands for clean energy, employing COFs as the sulfur hosts for providing sulfur cathodes in lithium-sulfur batteries has gained significant attention. In S-cathodes, the redox reaction occurs between  $\text{Li}^+$  and sulfur element leading to the generation of lithium polysulfides (LiPSs) which can migrate back and forth toward two electrodes. This shuttle effect can cause electrode passivation. So, immobilization of LiPSs *via* lithiophilic interactions can confine its transfer and boost Li-S battery performance. In one report, a quinoline-linked triazine-based COF was prepared from reversible imine linkage through aza-Diels-Alder cycloaddition. Owing to interactions of nitrogen atoms in triazine and quinoline moieties of the prepared COF with lithium polysulfides, it exhibited good electrochemical performance. Also, the extended  $\pi$ -conjugated structure of COF could facilitate electron transfer within Li-S conversion reactions.<sup>109</sup> In another effort, a Co coordinated tetrazole-functionalized benzoquinoline-linked COF was prepared in several steps to be employed as the Li-S battery cathode. At first, an imine-linked COF reacted with *p*-chloranil to form a

benzoquinoline-linked COF *via* the Povarov cycloaddition reaction. Then, the nitrile moiety in the benzoquinoline-linkage participated in further cycloaddition reaction with  $\text{NaN}_3$ . Finally, due to abundant nitrogen sites, this framework underwent coordination with Co salts to form target COF.<sup>110</sup>

**3.3.2. Hydrogen storage.** Considerable efforts are being carried out for the replacement of carbon-based fossil fuels with clean fuels in the transportation industry to avoid the emission of greenhouse gases. Hydrogen gas is a clean energy source that can be exploited for this aim. However, the lack of economical and safe  $\text{H}_2$  storage systems has limited the use of hydrogen fuel widely. Developing adsorption-based COFs for hydrogen storage is a utile method to overcome the restrictions. Post-treatment approaches including impregnation, Li-doping, and functionalization are effective methods for the enhancement of  $\text{H}_2$  adsorption ability in COFs. In one report, a combination of  $\text{C}_{60}$  impregnation or anchoring of an aromatic ring with Li-doping was employed for increasing  $\text{H}_2$  adsorption potency. Indeed,  $\text{C}_{60}$  impregnation can cause an expansion in framework surface area for additional Li-doping. Li-doped sites can interact with  $\text{H}_2$  molecules to bind them efficiently.<sup>111</sup>

**3.3.3. Proton-exchange membrane fuel cells.** Functionalized COFs are used as proton-conductive materials in proton-exchange membrane fuel cells. In these fuel cells, hydrogen gas is oxidized to protons at the anode and then, proton diffusion through the conductive membrane toward the cathode occurs. There protons attract electrons and electricity is produced. Water is the only by-product of this reaction. So, this is a clean method for energy generation.<sup>112</sup> In one research, sulfonic acid groups were grafted on COF walls *via* post-functionalization to obtain highly efficient proton-conductive COFs.<sup>113</sup> Also, the previously mentioned ionic COF showed unprecedented  $\text{H}^+$  conduction. This superior conduction is attributed to the hydrophilicity of  $\text{Li}^+$  or  $\text{Na}^+$  decorated COF which leads to promoting hydrogen-bond density between adsorbed  $\text{H}_2\text{O}$  molecules and mobile  $\text{H}^+$ . So,  $\text{H}^+$  motion is facilitated. Furthermore, the  $\text{H}_2\text{O}$  adsorption was evaluated *via* density functional theory-based molecular dynamics.<sup>66</sup> In

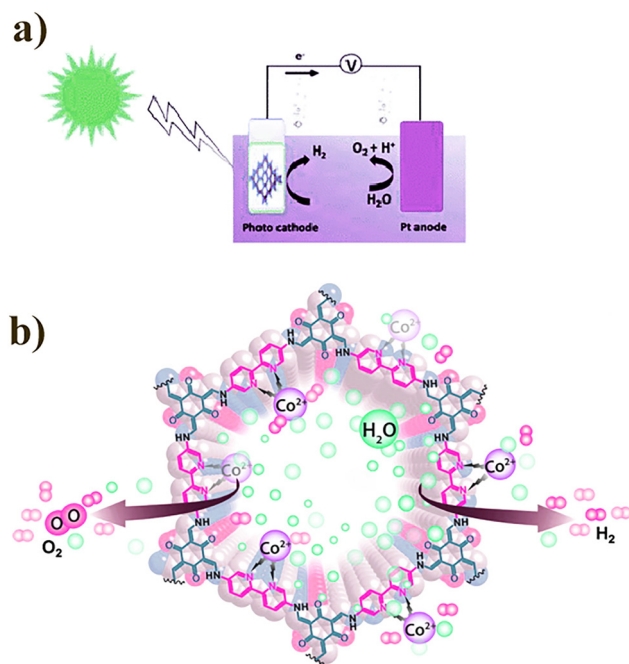
addition, a  $\beta$ -ketoenamine type COF was post-metalized with  $\text{CuCl}_2$  to design a novel extremely proton conductive COF, employed in fuel cell applications. Indeed, carbonyl and amine groups in the COF backbone provide chelating sites for introducing copper(II) ions into the platform.<sup>114</sup>

**3.3.4. Water splitting.** Photoelectrochemical (PEC) water splitting is a utile technique for hydrogen production, which has attracted the attention of researchers as a green energy source. Indeed, in this technology, solar energy is converted into chemical energy by splitting water into hydrogen (at the cathode) and oxygen (at the anode) in the presence of visible light. In other words, this electrochemical reaction consists of two half-cell reactions: the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). In PEC cells, electrocatalysts can accelerate the kinetics of both half-cell reactions, which leads to the improvement of PEC performance (Fig. 16(a)).<sup>115</sup> Metal atom dispersed materials are considered as attractive electrocatalysts for water oxidation. COFs due to their porous structure are excellent platforms for embedding metal atoms. Electrochemical water oxidation performance in the presence of previously mentioned metallophthalocyanine COFs was evaluated *via* cyclic voltammetry (CV).<sup>63</sup> In one study, a COF, containing bipyridine moieties, was post metalized with  $\text{Co(II)}$  ions to form an efficient OER electrocatalyst (Fig. 16(b)).<sup>116</sup>

### 3.4. Heterogeneous catalysts

Heterogeneous catalysts, due to their easy recycling ability and reusability are more preferred in industries than homogeneous

ones. As mentioned previously, three Pd-anchored COFs were designed as heterogeneous catalysts in a palladium-based Suzuki–Miyaura cross-coupling reaction. In this reaction, aryl halide reagent reacts with aryl boronic acid to obtain the bi-aryl compound. Although after grafting palladium onto the COFs, its oxidation state remains +2, Pd(0) is formed in a pre-step. Pd(0) plays a key role in a successful coupling reaction which consists of oxidative addition, trans metalation, and reductive elimination steps. Bidentate ligands with N–N-, N–O-binding sites, provide a higher coordination capability toward palladium than the monodentate one. However, the total rate of the coupling product formation is influenced by the conversion rate of Pd(II) to Pd(0) at the pre-step. As a result, among these three COFs, the one with N–O-binding sites was the best due to its fast kinetics and coordination strength.<sup>61</sup> Also, in another research, an efficient heterogeneous catalyst for progress in asymmetric Henry reaction has been offered. To gain this catalyst, a chiral auxiliary was grafted to pyridine-based COF through the reaction of pyridine units of COF with (S)-prolinol bromoacetate to form an organic cationic ionic liquid (OCIL)-based chiral COF. Henry reaction between nitromethane and substituted benzaldehydes in the presence of this catalyst demonstrated high yields (up to 97%) and stereoselectivity of 92% ee.<sup>117</sup> In addition, a heterogeneous photocatalyst has developed through dual metalation of a COF, bearing bipyridine binding sites, with iridium and nickel. This catalyst was used in C–N coupling reactions of various amines, sulfonamides, and carbamides with aryl iodides to diversify some drugs such as naproxen, ibuprofen, and  $\epsilon$ -aminocaproic acid with high yield. Indeed the enhanced catalytic activity is related to the proximity of two redox centers and electrons transferring between Ir and Nickel centers.<sup>118</sup> Furthermore, designing catalysts for the conversion of  $\text{CO}_2$  into inoffensive compounds is a favourable approach. A highly efficient bifunctional catalyst has been prepared by a nucleophilic substitution reaction between the pyridine moiety in the COF skeleton and  $\text{Br-CH}_2\text{-COOH}$  through a post-modification strategy. This designed catalyst had dual acidic ( $\text{COOH}$ ) and nucleophilic (anion  $\text{Br}^-$ ) catalytic sites and facilitated the cycloaddition reaction of  $\text{CO}_2$  with epichlorohydrin to construct cyclic carbonate (Fig. 17). To further investigate the influence of the nucleophilic site on the catalyst efficiency,  $\text{COOHCH}_2\text{Cl}$  and  $\text{COOHCH}_2\text{I}$  were used instead of  $\text{COOHCH}_2\text{Br}$  to synthesize COFs with  $\text{Cl}^-$  and  $\text{I}^-$  anionic sites respectively. According to the results these two COFs showed lower catalytic activity compared to the  $\text{Br}^-$  containing counterpart. The poor nucleophilicity of  $\text{Cl}^-$  and large radius of  $\text{I}^-$  which can limit the diffusion of reactants into the COF are responsible for these results. Moreover, this reaction in the presence of the COF with  $\text{COOH}$  and  $\text{Br}^-$  catalytic sites was expanded for use in  $\text{CO}_2$  conversion with various epoxides as showed in Table 1. With the increase in the size of epoxide, the catalytic activity of the COF decreased significantly which was attributed to the limited diffusion of bulky epoxides into the pores of the COF.<sup>119</sup> Also, other ionic COF-based catalysts for cycloaddition reactions between carbon dioxide and epoxides have been proposed.



**Fig. 16** (a) Mechanism of splitting water to hydrogen and oxygen in photoelectrochemical cells (reproduced with permission from ref. 115. Copyright 2022 The Royal society of chemistry). (b) The cobalt-coordinated COF as an electrocatalyst for water splitting (reproduced with permission from ref. 116. Copyright 2016 American Chemical Society).

## Highlight

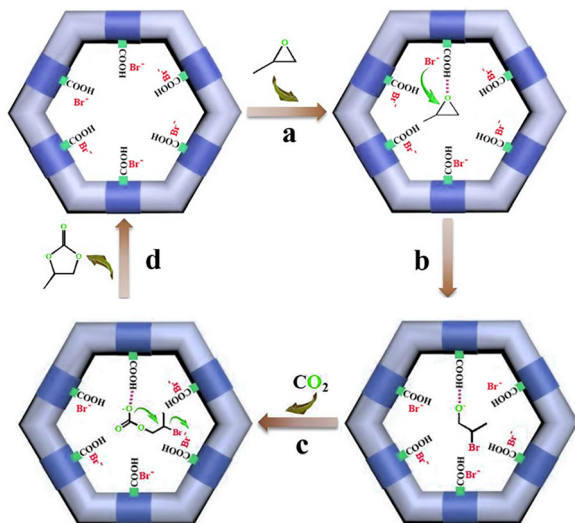


Fig. 17 Catalytic operation of the bifunctional COF for conversion of  $\text{CO}_2$  into carbonate (reproduced with permission from ref. 119. Copyright 2020 John Wiley and Sons).

Table 1 Reaction of  $\text{CO}_2$  with different epoxides in the presence of the bifunctional COF (reproduced with permission from ref. 119. Copyright 2020 John Wiley and Sons)

Entry	Catalyst	Epoxide	Substrate	Yield (%)
1	COF-TpPa-Py-Br <sup>-</sup>			61 ± 2.5
2	COF-TpPa-Py-Br <sup>-</sup>			10 ± 1.1
3	COF-TpPa-Py-Br <sup>-</sup>			3 ± 0.8

For instance, in another attempt, a cationic COF was formed *via* a two-step post-modification approach. At first, phenolic hydroxyl groups in the COF underwent Williamson etherification reaction with 1,4-dibromobutane and then, this alkyl bromide functionalized COF participated in nucleophilic substitution reaction with 1-methylimidazole.<sup>120</sup>

### 3.5. Food safety evaluation

Basic orange II is an azo dye. Although it is utilized for paper, cloth, and leather, it is prohibited as a food additive, due to its toxicity. The detection of this substance for the evaluation of food safety in the food industry has gained considerable attention. For example, in one attempt, a sodium sulfonate-anchored magnetic COF was suggested as an effective adsorbent in a magnetic solid-phase extraction (MSPE) strategy for

the determination of this dye in food samples. Hydrogen bonds, ion exchange, and  $\pi$ - $\pi$  interactions between dye and adsorbent are responsible for the selective adsorption toward basic orange II.<sup>121</sup> Also, per- and polyfluoroalkyl substances (PFASs) are exploited in the food industry as stabilizers for dairy products. Owing to high C-F bonding energy, these compounds are bioaccumulative and toxic. So, a cationic COF was prepared *via* quaternization of 2,2'-bipyridine moieties of COF with 1,2-dibromoethane for PFAS adsorption. Its adsorption capacity has been improved *via* electrostatic interactions.<sup>122</sup> Furthermore, endocrine disrupting chemicals (EDCs) can intervene with endocrine system operation *via* simulating or antagonizing the hormones of the body. So, the determination of trace amounts of these substances in food samples is vital. For this aim, a boric acid-grafted magnetic COF nanocomposite was prepared by using  $\text{Fe}_3\text{O}_4$  nanoparticles as the core and boric acid-anchored COFs as the shell. This sorbent demonstrated low limits of detection equal to 0.08–0.72  $\mu\text{g kg}^{-1}$  for EDCs in meat samples.<sup>123</sup>

### 3.6. Gas separation

Gas separation such as  $\text{CH}_4/\text{C}_2\text{H}_2$  separation is of great importance in the industry. For this aim, a quinoline-linked COF was obtained through an aza-Diels-Alder reaction between an imine-linked COF with an enamide, containing  $\text{CF}_3$  group. Also,  $\text{FeCl}_3$  was used as the catalyst. Due to the interactions between hydrogen atoms of  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$  molecules and fluorine or nitrogen atoms of the prepared COF, this post-modified COF is a promising candidate for  $\text{CH}_4/\text{C}_2\text{H}_2$  separation. Indeed it showed stronger interactions toward  $\text{C}_2\text{H}_2$ .<sup>124</sup> Moreover, due to the importance of efficient elimination of  $\text{CO}_2$  from natural gas and biogas, a polyethylene glycol monomethyl ether modified COF was used as filler for fabricating COF-based mixed matrix membranes (MMMs) to raise  $\text{CO}_2$  gas separation.<sup>125</sup> Also, in one study a modified COF-based MMM was prepared by post-impregnation of a COF with an amidazolium-based ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide ([bmim][Tf2N]). This membrane was employed for efficient  $\text{CO}_2/\text{CH}_4$  separation. Indeed, the anchored ionic liquid acts to maintain the roles in the preparation of this high-performance MMM. The first is the increase in the  $\text{CO}_2$  solubility of the membrane, arising from strong interactions between the ionic liquid moieties and  $\text{CO}_2$  molecules, and the second is the decrease in the pore size of the post-modified COF from 1.28 nm to 1.09 nm which can limit the diffusion of  $\text{CH}_4$  molecules with larger size than  $\text{CO}_2$  molecules.<sup>126</sup> Moreover, in a similar work, a COF membrane was loaded with a layer of ionic liquid containing silver ions and utilized for ethylene/ethane separation. The channel size of the initial COF membrane was 1.44 nm which was larger than the sizes of ethylene and ethane molecules (0.42 nm and 0.44 nm respectively). Therefore, both of them could be transported through the membrane readily, and the membrane selectivity toward them was low. After modification of COF with ionic liquid, the channel size reduced to 0.87 nm. Although this size was still larger than that of both molecules,

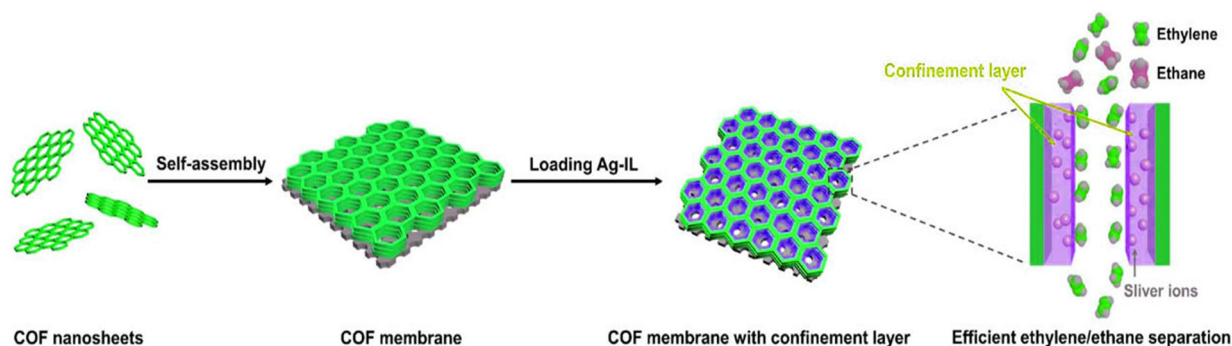


Fig. 18 The modified COF membrane for gas separation (reproduced with permission from ref. 127. Copyright 2022 The Royal society of chemistry).

the ethylene/ethane selectivity increased. The reason was ascribed to the bond formation between ethylene molecules and silver ions, presented in the ionic liquid, which led to the further reduction of the channel size to prevent the transportation of ethane molecules (Fig. 18).<sup>127</sup>

## 4. Conclusions and perspective

Post-synthetic modification (PSM) approaches including post-functionalization, post-metalation, chemical locking, and host-guest post-modification are helpful strategies for introducing functionalities into COFs when the direct synthetic approach cannot be employed. The PSM method leads to the improvement of COF features such as pore size, conductivity, stability, hydrophobicity/hydrophilicity, and chirality. Also, grafting different functionalities on COFs makes them suitable platforms for the adsorption of different environmental pollutants including, greenhouse gases, dyes, heavy metals, radioactive elements, oxoanions, carboxylic acid pesticides, and non-steroidal anti-inflammatory drugs. Also, functionalized COFs can be employed as biosensors, nanocomposites for drug delivery, and chiral stationary phases of chromatography columns for gaining enantiopure drugs. In addition, their applications in various fields such as producing clean energy, heterogeneous catalysts, evaluating food safety, and gas separation are taken into consideration. Due to the recent promising progress of this synthetic approach, it is expected that further restrictions in the synthesis of functionalized COFs with tuned features will be removed with further diversifying of these post-modifications in the future. In other words, the PSM strategy development will lead to innovations in the design of functionalized COFs and dealing with the problems in direct synthetic methods. Moreover, according to the reported literatures, it is concluded that functional groups, grafted on the COFs can participate in different interactions such as hydrogen bonding, hydrophobicity,  $\pi$ - $\pi$ , coordination and electrostatic interactions with other molecules to capture them. Also, these functionalities can affect the affinity of COFs toward various molecules by tuning of the pore wall size. These molecules include a wide range of substances from gases and pollutants to drugs and biological molecules or even ions. Therefore, these

functionalized platforms can make further progress in sensors, adsorbents, drug delivery systems, conductive materials and some other fields in the future. Despite all mentioned merits of PSM methods, there are still some troubles which have limited the use of PSM strategies. For instance, multi-step reactions in PSM approaches are tedious and complicated, resulting in a waste of time, energy, and materials. Also, the large-scale production of functionalized COFs for different applications with multi-step reactions is limited. One-pot PSM approaches are conversely economical. However, most of the post-modifications, which have been reported so far, are based on multi-step reactions and there is an urgent demand for improving one-pot reactions. In general, improving these strategies requires more recognition of them and their potential in various fields. Therefore, there is much room for working on this domain.

## Conflicts of interest

There are no conflicts to declare.

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