Fully Conjugated Covalent Organic Frameworks: Synthesis, Structures and Applications

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Abstract

This review presents a comprehensive examination of fully conjugated covalent organic frameworks (COFs), which constitute an emerging class of porous materials with immense potential for diverse applications. This article focuses on diversified fully conjugated COFs, including sp2 carbon-carbon linkages, pyrazine linkages, benzobisoxazole linkages, dioxin linkages, β-aminoalkenone linkages, etc. The synthesis techniques and structural attributes of these COFs are expounded upon in great detail, along with their potential applications in various fields. The review thus provides a valuable resource for researchers keen on delving into the synthesis and applications of fully conjugated COFs, thereby highlighting their potential for developing novel functional materials with distinctive properties.

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Keywords

Covalent organic frameworks | Fully-conjugated system | Crystallinity | Stability |

Comprehensive Summary

This review presents a comprehensive examination of fully conjugated covalent organic frameworks (COFs), which constitute an emerging class of porous materials with immense potential for diverse applications. This article focuses on diversified fully conjugated COFs, including sp2 carbon-carbon linkages, pyrazine linkages, benzobisoxazole linkages, dioxin linkages, β-aminoalkenone linkages, etc. The synthesis techniques and structural attributes of these COFs are expounded upon in great detail, along with their potential applications in various fields. The review thus provides a valuable resource for researchers keen on delving into the synthesis and applications of fully conjugated COFs, thereby highlighting their potential for developing novel functional materials with distinctive properties.

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Left to Right: Yueshuai Xu, Guanshi Ren, Dianqi Zhang, Lishui Sun, Yingjie Zhao

Contents

1. Introduction Page No.2
2. sp² carbon-carbon Linkages Page No.3

2.1. Aldol reaction Page No.3

2.2. Knoevenagel reaction Page No.6

3. Pyrazine Linkages Page No.14

4. Benzobisoxazole Linkages Page No.14

5. Dioxin Linkages Page No.16

6. β-Amino Enone Linkages Page No.17

7. Post-Synthetic Modification Page No.17

8. Multicomponent One-Pot Reaction Page No.19

9. Conclusions and Perspectives Page No.20

1. Introduction

COFs have gained significant attention due to their highly ordered structures and precise design and synthesis.[1-5] These crystalline, porous two or three-dimensional networks have accurately porous structures that make them useful for gas storage and separation, heterogeneous catalysis, and drug delivery.[6-11] To synthesize these highly ordered structures, reversible dynamic covalent bonds as linkages between building blocks are usually necessary.[12-14] The mostly used linkages for constructing COFs are limited to B-O and C=N bonds, which have a well-known self-adjusting property that facilitates the formation of well-ordered structures.[15-19] However, these bonds usually have poor stability and weak electron delocalization, which sacrifices chemical stability and conjugation. This limitation restricts their application in fields such as organic semiconductors, photocatalysis, and ferromagnetic materials, which require high π-electron delocalized systems.[20-23] To overcome these limitations, many efforts have been made to explore new chemistry to construct highly stable and electron-delocalized COFs. However, constructing fully conjugated COFs requires new linkages with poor reversibility, which is unfavorable for the crystallinity. A perfect equilibrium point is needed to maintain both the crystallinity and conjugation (Figure 1). Although fully conjugated COFs are fascinating materials, keeping the crystallinity is an extremely challenging job because the reversibility of the conjugated bond is usually bad, which is unfavorable for self-adjusting.[24-28]

In this review, we focus on the recent progress of COFs with new linkages beyond the common B-O and C=N bonds and holding fully conjugated structures. Fully conjugated COFs with new linkages or obtained through new chemistry synthetic strategies were included. The potential applications of these COFs, including gas storage and separation, heterogeneous catalysis, and drug delivery, were also summarized.[29,30] Finally, we present an outlook on the future development of these COFs, which includes exploring new chemistry strategies for constructing stable, highly ordered COFs with excellent π-electron delocalization and porosities suitable for various applications.[31-34]
2. \textit{sp}^{2}\textit{carbon-carbon Linkages}

The fully conjugated COFs constructed with new linkages beyond borate and imine bonds are still less reported. The most published examples of fully conjugated COFs focus on \textit{sp}^{2} carbon-carbon linked COFs (\textit{sp}^{2}c-COFs), which possess conjugated structures connected by \textit{sp}^{2} carbon-carbon bonds. Compared to the traditional imine-based COFs, the \textit{sp}^{2}c-COFs have excellent stability and semiconductor properties and have shown a wide range of applications, including catalysis, sensing, separation, energy storage, conversion, etc. Typically, the most used synthetic reactions for the preparation of \textit{sp}^{2}c-COFs focus on the Aldol and the Knoevenagel reactions.

2.1. Aldol reaction

Zhang and co-workers successfully fabricated a series of \textit{sp}^{2}c-COFs utilizing pyridine units as the central building block via the Aldol reaction. The autocatalytic acylation of the pyridine unit by common acylation reagents, such as acetic acid, anhydride, or acyl halide, can promote the growth of vinylidene chains. Based on this strategy, a series of COFs constructed by vinylidene linkages (\textbf{COF-1}, \textbf{COF-2}) can be successfully synthesized (Figure 2a).\textsuperscript{[35]} Notably, these COFs exhibit intriguing spatially restricted catalytic activity towards the esterification reactions of certain crucial drug intermediates, demonstrating high yields, remarkable recoverability, and reusability, as well as excellent selectivity. Subsequently, the same group reported another two \textit{sp}^{2}c-COFs (\textbf{COF-3} and \textbf{COF-4}) with an orthogonal reticulation topology through a
condensation reaction between a tetradentate monomer and a dichotomous linear aromatic dialdehyde (Figure 2b).\[^{36}\] The presence of the pyridine unit has the capacity to facilitate the condensation reaction through the decomposition of the benzoic anhydride molecule. The obtained COFs exhibit exceptional characteristics such as high crystallinity and porosity. The remarkable semiconducting properties and corresponding applications of both COFs can be attributed to the \(\pi\)-extended conjugated backbone made by the bipyridine unit and the vinylidene linkages in the COFs.

Zhang and co-workers further used 1,3,5-trimethyl-2,4,6-tricyanobenzene as a monomer to construct a series of sp\(^2\)-c-COFs (COF-5, COF-6, COF-7) (Figure 3).\[^{37}\] These COFs exhibit high specific surface area and excellent semiconductor properties, including superior \(\pi\)-domain separation, dense light-trapping ability, and tunable band structure. They were also found to be efficient in catalyzing the oxidation of aryloboric acids to aryl phenols in a wide range of substrates at low loading and short reaction times. The same group reported another series of sp\(^2\)-c-COFs (COF-8 to 11) by using 3,5-dicyano-2,4,6-trimethylpyridine as the key building block and linear/trigonal aldehydes (Figure 4).\[^{38,39}\] A systematic analysis of the photophysical and electrochemical properties of COF-8, COF-9 and COF-10 has been conducted. Among these sp\(^2\)-c-COFs, the highly crystalline COF-10 has been highlighted as an exemplar and analyzed in detail. The cyano-pyridine cores and the fully-\(\pi\) conjugated stable C=C bond endow COF-10 with excellent light-harvesting characteristics and stable \(\pi\)-electron delocalized properties. Thus, the COF-10 can act as a stable photocatalyst and be capable of hydrolysis in two half-reactions in the presence of sacrificial agents, achieving high hydrogen generation yields. In another example, the cyano-pyridine and the triazine cores work together with the fully-\(\pi\) conjugated stable C=C bond in COF-11, allowing the generation of uninterrupted \(\pi\)-electron leaving domains in the 2D direction. Notably, a unique nanofibrous morphology was obtained for COF-11. The assembly of COF-11 with carbon nanotubes allows easy access to flexible thin film electrodes for micro-supercapacitors.

The synthesis of ionic sp\(^2\)-c-COFs (COF-12 and COF-13) was also successfully realized by combining the ionic monomer with multiple aromatic aldehydes by Zhang and co-workers (Figure 5).\[^{40}\] These COFs are able to be composited uniformly with polyethylene oxide and lithium salts and exhibit good ionic conductivity due to their regular and persistent nanochannels and the unique charged framework. Zhang and co-workers further reported two novel 2D sp\(^2\)-c-COFs (COF-14 and COF-15) through Aldol reaction by using 2,4,6-trimethyl-1,3,5-triazine as the central unit (Figure 6).\[^{41}\] The fully \(\pi\)-conjugated 2D structures of these two COFs bring excellent semiconductor properties such as visible-light harvesting ability and charge separation ability. These properties endow them with visible-light-driven photocatalytic activity for the decomposition of water to produce hydrogen. Notably, COF-14 and COF-15 can also be assembled into microfibrous forms like the example discussed.

![Figure 2. The synthesis and structures of COF-1 to COF-4](image-url)
Figure 3. The synthesis and structures of COF-5 to COF-7

Figure 4. The synthesis and structures of COF-8 to COF-11
above, which allows them to be fabricated in micron-thick films without any additives. In particular, the COF-14 film shows a photocurrent of up to 45 μA cm⁻² and rapid interfacial charge transfer at 0.2 V vs RHE. It also exhibited an apparent quantum yield of 1.06% in the 420 nm photocatalytic hydrogen precipitation reaction with a hydrogen yield of 14.6 μmol h⁻¹.

Perepichka and co-workers also reported the preparation of highly crystalline sp²-c-COFs from 2,4,6-trimethyl-1,3,5-triazine and aromatic dialdehydes. COF-16, COF-17 and COF-18 were obtained through a base-catalyzed procedure and exhibited high fluorescence and crystallinities (Figure 7). Among these three COFs, COF-16 is highly hydrophilic, showing multiple expansions in volume when it was in contact with protonic solvents (e.g. water). Notably, this behavior was not observed in the amorphous samples. This observation is significantly different from the hydrophobic behavior of most reported COFs, including triazine-based microporous polymers. Subsequently, they realized the transition from crystalline ethylene-linked 2D COFs to crystalline cyclobutane-linked 3D COFs through the illumination of COF-16 and COF-17 (Figure 7). Specifically, the absorption edge irradiation of sp²-c-COFs leads to topological [2+2] cycloaddition crosslinking of π-stacked layers in 3D COFs. And the crosslinking between the COFs layers can be reversed by heating the COFs to 200 °C, thereby opening the strained cyclobutane rings and restoring the polyolefin network. The induced differences were probed by optical (absorption,
Figure 6. The synthesis and structures of COF-14 and COF-15

luminescence) spectroscopy and acid doping measurements. The effect of 2D-3D conversion on the gas adsorption, dephasing and ion (Li\(^+\), H\(^+\)) transport properties of COFs was further elucidated.

Yaghi and co-workers obtained an unsubstituted sp\(^2\)c-COFs (COF-19) by Brønsted acid-catalyzed reaction between 2,4,6-trimethyl-triazine and 4,4’-biphenyldialdehyde (Figure 8).\(^{44}\) Due to the chemical stability of the olefin linkages, COF-19 was found to maintain its crystallinity and chemical composition in the presence of highly concentrated Brønsted acids and bases, organolithium reagents, and Lewis acids. The chemical stability realizes the immobilization of Lewis acid catalysts in the pores of the COFs. And they also confirmed the activity of the Lewis acid-based-COF catalyst through the successful catalysis of the Diels-Alder reaction.

Thomas and co-workers reported two sp\(^2\)c-COFs (COF-20 and COF-21) by exploiting the electron-deficient nature of 2,4,6-trimethyl-triazine (Figure 8).\(^{45}\) The acidic terminal methyl hydrogen of 2,4,6-trimethyl-triazine can be readily extracted by a base, resulting in a stable carbon ion that further undergoes an aldol condensation with polythematic aromatic aldehydes to form reticulated extended crystal frameworks. This work demonstrates that crystallization of 2D vinyl-linked COFs can be achieved by using highly electron-deficient s-
triazine nuclei under alkali-catalyzed conditions. By using UV-Vis irradiation of COF-20 powders, they observed that \([2+2]\) photocycloaddition reaction within the \(\pi-\pi\) stacked layer of the 2D columnar COFs. The COF-20 remains crystalline after light irradiation due to the formation of highly strained cyclobutane rings within the 2D layers. This is because the pre-organized vinylidene in the adjacent 2D layer of COF-20 provides a platform for \([2+2]\) cycloaddition under UV-Vis irradiation, satisfying Schmidt’s criteria for photocyclization.

**Figure 7.** The synthesis and structures of COF-16 to COF-18
Figure 8. The synthesis and structures of COF-19 to
COF-21

The same group then reported a series of sp\(^2\)c-COFs (COF-20, COF-21, COF-22) by using a different synthetic strategy through acetonitrile as monomers (Figure 9). This method provides a description of the acid-catalyzed synthetic pathway for vinylidene-linked COFs and avoids the side reactions associated with the base-catalyzed synthesis. A nitrile trimerization reaction with an Aldol reaction was adopted through a two-step, one-pot reaction. The universality of this synthetic strategy was further verified by the successful preparation of four different COFs (COF-19, COF-20, COF-21 and COF-22).\(^{46}\)

Zhang and co-workers developed a solvent-free synthetic strategy that is similar to the melt polymerization process. COF-23 was successfully synthesized through an Aldol reaction between the 2,5-dimethylpyrazine and 1,3,5-tricarbonylbenzene under solvent-free conditions (Figure 10). Subsequently, the H\(_3\)PO\(_4\)@COF-23 complex was further constructed by anchoring the proton carrier H\(_3\)PO\(_4\) inside the pores of COF-23.\(^{47}\) Under usual fuel cell operating conditions, it exhibited ultra-high proton conductivity and excellent performance as a solid electrolyte membrane. By using this solvent-free and melt polymerization strategy, the same group further synthesized a series of highly crystalline sp\(^2\)c-COF (COF-24, COF-25, and COF-26) through 2,4,6-collidine and xylene as the monomer (Figure 10).\(^{48}\) This method enabled the fabrication of COFs with self-contained and robust foams at the kilogram scale. The obtained COFs have an extremely low cost (< $50 / kg). In addition, neutral COFs can be easily converted to ionic COFs by using one-pot or post-modification methods, which can be used as efficient ion-exchange sorbents for the removal of oxygen ion contaminants. This work not only expands the range of olefin-linked COFs but also enlightens the route to industrial production of crystalline ion-exchange adsorbents.

2.2. Knoevenagel reaction

Feng and co-workers reported the synthesis of three sp\(^2\)c-COFs (COF-27, COF-28, and COF-29) by utilizing 2,3,8,9,14,15-hexa(4-formylphenyl)diquinoxalino[2,3-a:2',3'-c]phenazine (HATN-6CHO) as the building block (Figure 11). In comparison to their imine-linked COF analogs, COF-29 demonstrates superior chemical and electrochemical stability, rendering it a more promising candidate for practical applications.\(^{49}\) To further enhance the electrical conductivity of COF-29, an in-situ growth on carbon nanotubes was employed to generate a core-shell hybrid material (COF-29@CNT).

Figure 9. The synthesis and structures of COF-19 to COF-22
Figure 10. The synthesis and structures of COF-23 to COF-26

This hybrid material was then utilized as a cathode material for lithium-ion batteries (LIBs) and demonstrated remarkable performance, including a high capacity of 116 mA h/g and exceptional cycling stability. Furthermore, the double thiophene-bridged COF-27 exhibited a narrower optical energy band gap (2.04 eV), a higher LUMO energy level (~3.41 eV), and improved charge separation and transport in contrast to biphenyl-bridged COF-28 and 2D C=N COF-B, attributed to the D-A structure. COF-27 also demonstrated exceptional photocathode activity in photoelectrochemical devices with an excellent saturation photocurrent density for water reduction.

In 2016, Feng and co-workers reported the successful synthesis of sp^2-COFs (COF-30) by using Knoevenagel polycondensation between 1,4-benzene diacetonitrile and 1,3,5-tris(4-formylphenyl) benzene as the monomers (Figure 12). The obtained COF-30 exhibits a crystalline lamellar structure with a fully-π conjugated sp^2-carbon bonded skeleton and pendant cyano groups. PXRD studies and theoretical simulations verified the 2D structure. The nitrogen physisorption measurements give a specific surface area of as high as 880 m^2 g^-1. Remarkably, COF-30 exhibited substantial potential for application as supercapacitor electrodes and electrocatalysts in oxygen reduction reactions.

The same group furthermore developed a new strategy for the synthesis of sp^2-COFs, which employed Knoevenagel polycondensation in conjunction with water-assisted Michael addition elimination. The successful synthesis of a series of sp^2-COFs (COF-28, COF-31 and COF-32) strongly supports the universality of this strategy (Figure 11, 12). An in-situ high-temperature NMR measurement was utilized on the model reaction and intermediate to distinguish Michael-addition elimination from the hypothetical reversible Knoevenagel reaction. Furthermore, water-assisted Michael addition elimination was identified as effective dynamic covalent chemistry for direct C=C bond exchange, which endowed self-correcting properties for synthesizing extended structures. Consequently, Michael addition elimination polymerization was demonstrated to be an efficient approach for the synthesis of sp^2-COFs with high crystallinity.

Zhao and co-workers present the successful synthesis of an sp^2-COF (COF-31) with a triazine moiety serving as the central planar unit (Figure 12). In order to enhance electron delocalization, olefin (-C=C-) bonds were utilized instead of the commonly used imide (-C=N-) bonds as sp^2-carbon bridges. The resulting sp^2-carbon bonds endowed the COF-31 with superior stability and electron delocalization. Furthermore, the incorporation of the triazine unit as a functional moiety positively modulated the electronic structure and semiconductor properties of COF-31, making it a promising photocatalytic candidate for photosystem I-like
systems. To demonstrate the potential of COF-31 in catalysis, COF-31 was employed to catalyze coenzyme regeneration, resulting in a remarkable glutamate synthesis yield of 97% in 12 min. These findings highlight the potential of COF-31 as an efficient photocatalyst and offer promising avenues for future research in the field of catalysis.

In 2022, Liu and co-workers reported an efficient gradient heating strategy for the preparation of COF-31, resulting in the creation of a material with high crystallinity and a large surface area (Figure 12). This material has demonstrated remarkable properties, including high crystallinity, large surface area, excellent durability, and carrier mobility, rendering it particularly suitable for solar-driven photocatalytic hydrogen production. Notably, when triethanolamine or ascorbic acid are utilized as sacrificial electron donors, platinum-doped COF-31 exhibits unexpectedly high activity in both photocatalytic systems.

Figure 11. The synthesis and structures of COF-27 to COF-29

Figure 12. The synthesis and structures of COF-30 to COF-34

Qiu and co-workers reported the synthesis of sp²-COF (COF-34), which exhibits excellent stability towards chemical, thermal, and radiation exposure (Figure 12). The incorporation of amidoxime ligands in the
open one-dimensional channel imparts selective binding of UO$_{22}^{2+}$ ions. Furthermore, COF-34 exhibits an ultra-fast response time of 2 seconds and an ultra-low detection limit of 6.7 nM UO$_{22}^{2+}$. These properties make COF-34 an ideal candidate for in situ and real-time monitoring of UO$_{22}^{2+}$ and assessment of water quality, besides its potential application in UO$_{22}^{2+}$ extraction.$^{[56]}$

Jiang and co-workers reported a series of sp$^2$-c-COFs (COF-35, COF-36, COF-37, and COF-38) utilizing pyrene as the central structural moiety through the Knoevenagel condensation reaction (Figure 13). The systematic investigation of the structures, applications, mechanisms, and synthesis methods of these sp$^2$-c-COFs has been extensively discussed. Among these COFs, COF-35 features a topologically oriented mesh structure in which C=C linkages connect the pyrene nodes at regular intervals to form a π-conjugated 2D lattice that extends in the x and y directions.$^{[57]}$ The overlapping layers of this lattice form a highly stable framework. COF-35 possesses semiconductor properties and exhibits a discrete band gap of 1.9 eV. Through chemical oxidation, the electrical conductivity of J-COF-1 can be significantly increased by up to 12 orders of magnitude.

The COF-35, COF-36, and COF-37 were then found to exhibit exceptional stability.$^{[58]}$ Furthermore, they observed that the linkers adopt propeller conformation to constitute twisted arylenevinylene backbones. As a result, the π-domain transport of the COF-35, COF-36, and COF-37 along the x and y directions can be regulated by the linker unit, facilitating the adjustment of the band gap and emission color. The researchers have demonstrated the structure-light function correlation in this study, indicating that photochemical events are highly correlated with the first and higher-order structures of the sp$^2$-c-COFs by elucidating the structural parameters that govern the photochemical events.

In the subsequent studies, it is discovered that the COF-35 possesses a distinctive combination of π-conjugation, crystallinity, porosity, and photostability that allows it to absorb a broad spectrum of light and maintain a steady H$_2$ release rate of 1360 mmol/[?]h$^{-1}$/[?]g$^{-1}$ from water. In order to further enhance light absorption and narrow the band gap, the researchers integrated an electron-deficient 3-ethyl-rhodanine (ERDN) unit as an end-cap group into the periphery of the COF-35 lattice, resulting in the synthesis of COF-38 (Figure 13).$^{[59]}$ The present framework embodies a light-driven photocatalytic system, wherein a sequence of photocatalytic phenomena comprising light absorption, exciton migration, exciton separation, electron transfer, and charge collection are intimately interconnected and function in tandem. This integrated mechanism engenders the capability of sp$^2$-c-COFs to achieve sustained and efficient hydrogen evolution from water, utilizing a broad spectrum of visible-to-near-infrared radiation.

To further optimize the optical and optoelectronic functionality of the obtained 2D sp$^2$-c-COFs, a thorough understanding of the emitting and non-radiative pathways following photoexcitation is crucial and should be linked to specific structural designs. Jiang and Scholes employed transient absorption spectroscopy to examine the colloidal suspension of COF-35, and to characterize the spatial extent and diffusion kinetics of emitting excitons produced by pulsed photoexcitation. A stacking distance of 3.5 Å between the 2D layers results in the diffusion of coplanar pyrene excitons within the framework, while the dominant polycrystalline solid emission spectrum state is attributed to an extended coplanar exciton whose two-dimensional off-domain is facilitated by a C=C connection. The sub-nanosecond dynamics of the photo-induced absorption signal in the near-infrared, which is attributed to charge-separated excitons or multiple pairs, reflects 3D exciton diffusion as well as long-range exciton-exciton annihilation driven by resonance interactions. In their experimental regime, doubling the excitation intensity results in a tenfold increase in the estimated exciton diffusion length from approximately 3 to 30 nm, suggesting that higher lattice temperatures may enhance exciton mobility in COFs colloids.$^{[60]}$

Cooper and co-workers reported an sp$^2$-c-COF (COF-39) containing bipyridyl and its post-synthetic modification through the introduction of rhenium (Figure 13).$^{[61]}$ In the presence of COF-40, excellent photocatalytic CO$_2$ reduction performance was exhibited. The COF-40 achieved a CO production rate of 1040 mmol g$^{-1}$ h$^{-1}$ under 17.5 h of light CO production rate with a selectivity of 81% for H$_2$. This performance was improved by 84% in 5 hours by dye sensitization, resulting in a CO production rate of 1400 mmol g$^{-1}$ h$^{-1}$ and a CO/H$_2$ selectivity of 86%. Based on a range of experimental and computational techniques.
Zhao and co-workers reported three sp²c-COF (COF-41, COF-42, and COF-43), which incorporate benzobisthiazole as an electron-withdrawing group, resulting in an electron-deficient π-conjugated C2-symmetric building block in combination with a cyano ethylene bond (Figure 14). Moreover, C3 symmetric units such as triazine and benzotrithiophene were introduced into the COFs skeleton as photoactive functional groups. The electronic properties of the C3 symmetric unit can be modified through the structure adjustment, allowing modulation of the semiconductor properties of the π-conjugated COF. COF-43, which contains electron-rich benzotrithiophene as a donor, exhibits a strong donor-acceptor (D-A) effect, leading to excellent photocatalytic hydrogen evolution reaction activity of 15.1 mmol/h⁻¹g⁻¹ under visible light irradiation. This performance is superior to that of COF-41 containing triazine (10.5 mmol/h⁻¹g⁻¹) and benzene-containing COF-42 (1.2 mmol/h⁻¹g⁻¹), which demonstrates that the sp²c-COF material with a D-A system has remarkable photocatalytic hydrogen evolution reaction performance. Furthermore, this work presents a facile method for the preparation of 2D sp²c-COFs through Knoevenagel condensation, where neutral AcONH₄ is used to catalyze the condensation.

Figure 13. The synthesis and structures of COF-35 to COF-40

Figure 14. The synthesis and structures of COF-41 to COF-43

thereby improving the reversibility of the initial step. This approach simplifies the traditionally challenging preparation and synthesis of sp²c-COFs.

The approach of polymerization via a template, as proposed by Jiang and co-workers, offers a convenient pathway toward the synthesis of sp²c-COFs. The study revealed that the imine-linked COFs are capable of seeding the C=C bond formation reaction and confining the growth of all sp² carbon lattice onto the x-y plane, so that the polymer chains can nucleate into the same topological tiling to form 2D all sp² carbon conjugated COFs. Through this method, a series of sp²c-COFs (COF-30, COF-35, and COF-44) were successfully
synthesized, each exhibiting tetragonal, hexagonal, and Kagome topologies (Figures 12, 13, and 15).\textsuperscript{[63]} The use of template aggregation provides a structural foundation for unraveling the unprecedented functionalities of $\pi$ transport and exciton leap in the two-dimensional sp$^2$ carbon backbone, which is controlled by the lattice topology.
Figure 15. The synthesis and structures of COF-44

In 2022, Jiang and co-workers developed a module-patterned polycondensation strategy for the efficient and designed synthesis of crystalline porous covalent organic frameworks. This strategy uses four branching segments as knot modules, and these knots with different π backbones can polymerize with different linkers, thus easily producing crystalline porous COFs in high yields. And it is widely applicable to a broad diversity of both knot and liker units with different structures, enabling the construction of a diversity of unprecedented crystalline 2D polymers and open frameworks. A series of sp²-c-COFs (COF-45 to COF-53) were successfully synthesized (Figure 16). The adaptable nature of C2-symmetric junction modules, which can be extended to comprise distinct π-skeletons and paired with varying linker units, engendered the creation of an unparalleled library of 2D sp²-carbon polymers and open frameworks.

Gu and co-workers reported an approach to synthesize cyano-substituted benzofuran bonded sp²-c-COFs via hydroxybenzaldehyde and acetonitrile building blocks. Two cyano-substituted benzofuran-linked skeletons (COF-54 to COF-57), which possess both crystallinity and porosity, were successfully prepared (Figure 17). In the initial process, Knoevenagel condensation generates the backbone reversibly, while successive cyanide migration, ring closure, and oxidation reactions produce irreversible heterocyclic cyano-substituted benzofuran bonds. This advancement extends the synthesis of sp²-c-COFs by integrating crystallinity, porosity, and post-synthetic modification feasibility into a chemically robust framework using irreversible reactions. The high stability of the benzofuran bond allows for the introduction of new functionality through post-synthetic modifications under harsh conditions. In a demonstration of its proof-of-concept, the acidified COF-57 displayed a remarkable super protonic conductivity of $4.35 \times 10^{-2}$ S cm⁻¹, thereby substantiating the viability and practical utility of COF materials of this nature.

Cui and co-workers reported two chiral sp²-COFs (COF-58 and COF-59) with a 2D lamellar tetragonal structure, employing olefin linkages as building blocks (Figure 18). Reduction of the olefin linkages of the prepared COFs generated C-C single bonds linked frameworks, which maintained high crystallinity, porosity, and superior chemical stability even in strongly acidic or basic conditions. The newly formed C-C bond linkage led to a blue-shifted emission, enhanced quantum yield, and fluorescence lifetime compared to the original structure. Furthermore, the enantioselectivity of the sp²-COFs was higher than its reduced structure when utilized as a fluorescent sensor for chiral amino alcohols. This study highlights the potential of utilizing COFs with tunable chemical and structural properties for the development of advanced materials with tailored properties.
The 2D sp$^2$c-COFs often encounter a bottleneck in charge transport between the layers. In this case, 3D sp$^2$c-COFs offer extended π-conjugation in the x, y, and z directions simultaneously, making them more favorable for charge transport in theory. However, the examples of reported 3D COFs have fallen far behind that of 2D COFs since Yaghi reported the first example of 3D COFs in 2007. Cao and co-workers reported an example of 3D sp$^2$c-COFs. Cyclooctatetra thiophene was utilized as a building block to construct this 3D sp$^2$c-COFs (COF-62) (Figure 19). The highly ordered nature of I$_2$-doped COF-62 led to an enhanced Hall
electron mobility of up to 2.62 cm$^2$V$^{-1}$ s$^{-1}$ in ambient air, which typically exhibits ferromagnetism without metals.

Fang and co-workers synthesized two 3D sp$^2$-COF$s$ (COF-63, COF-64) by using tetra4-formyl phenylene)silane as the central building block (Figure 19).$^{[68]}$ The potential application of COF-64 with a larger pore as a cancer drug (cisplatin, CIS) carrier is also explored. Furthermore, materials relating to the carrying of drugs (CIS@COF-64) not only functioned as a good drug-carrying and slow-release material but also as a potential cellular fluorescent dye that provided a long-lasting fluorescent tracer for drug transport.

Figure 19. The synthesis and structures of COF-62 to COF-68
Qiu and co-workers constructed a 3D COFs electroextraction platform for uranium adsorption from seawater. A 3D sp²-COF (COF-65) was synthesized through post-synthetic modification with ketamine oxime (Figure 19). After functionalization with an alkylamine oxime group, COF-66 was obtained, which exhibited a high affinity for uranyl ions. Under the action of an electric field, a strong sorption capacity...
toward uranyl ions was obtained.

Zhao and co-workers synthesized COF-67 through [3+4] imine condensation reaction. COF-67 was then transformed into quinoline-linked COFs (COF-68) (Figure 19). The nitrogen-riched triazine and pyrazine fractions in COF-68 can bind Li ions and provide multiple ion-adsorption active sites and ion storage space. The LIBs assembled with COF-68 electrodes demonstrated high Li-ion storage capacity and good cycling stability due to high chemical stability, π-conjugation, and good electronic and ionic conductivity.

3. Pyrazine Linkages

Pyrazine-linked COFs are usually constructed through the reaction of Pictet-Spengler between 1,2-cyclohexanedione and 1,2-phenylenediamine. The pyrazine linkages bring uninterrupted π-electron conjugation and make them a promising material for semiconductor applications. Jiang and co-workers reported a chemically stable π-electron-conjugated COF-69 (Figure 20). COF-69 with uninterrupted π-electron conjugation, which extends throughout the entire sheet of COFs, exhibits exceptional physical properties and three-dimensional periodic ordering that are typically absent in conjugated polymers.

The same group integrated cobalt (II) phthalocyanine into 2D COFs (COF-70) via a robust phenazine bond formation (Figure 20). Excellent stability, even under boiling water, acid, or base conditions, was obtained. COF-70 can be used as an electrocatalyst which is unique in its ability. By integrating all-π conjugated, stable backbone and catalytic sites into a single lattice, COF-70 exhibits excellent stability, conductivity, and catalytic activity in catalyzing the reduction of CO₂ to CO in water.

Hoberg and co-workers reported a series of COFs (COF-71 to 73) that possess highly stable semiconducting aromatic backbones and intrinsically ordered nanoscale pores (Figure 20). This family of COFs can be functionalized either through the monomer design and synthesis or the post-modification of the obtained COFs to incorporate various desired functional groups. This new bottom-up approach has achieved the objective of producing highly ordered and modifiable materials with stable aromatic backbones and functionalized pores. The condensation of readily available small precursor molecules in combination with well-established high-yield coupling reactions enables the replacement of the bromine placed on the aromatic ring of aligned pores, resulting in different functionalities.

Feng and co-workers reported a family of pyrazine-linked metal-phthalocyanine-based conjugated 2D COFs (COF-74-M, M = Zn, Cu, Ni) that assemble in van der Waals (vdWs) layer stacking structures (Figure 20). This work emphasizes the potential of fully conjugated 2D COFs with high mobility as optoelectronic semiconductors and provides a rational methodology for determining structure-property relationships. This work provides a dependable route to designing and developing semiconductor COF materials with enhanced charge transport properties.

The synthesis of fully conjugated COFs through the condensation reactions of various building blocks has resulted in the production of diverse materials with tunable properties. Mirica and co-workers investigated enhanced proton transport properties of COFs through the systematic study of two aza-COF analogues (COF-75 and COF-76) (Figure 21). The chemical composition, porosity, and crystallinity of these materials were found to play important roles in their proton transport properties, providing insight into the design and optimization of COFs for proton conduction.

Chen and co-workers reported the synthesis of a honeycomb-shaped nitrogen-rich COF (COF-77) with multiple carbonyl groups through a triple condensation reaction (Figure 21). This study also led to the discovery of materials with excellent electrochemical properties. COF-77 electrode demonstrated a high specific capacity, excellent cycling stability, and good rate capability, making it a promising candidate for use in high-energy and high-power sodium batteries. This work highlights the potential of COFs with multiple redox sites as high-performance electrode materials and provides a basis for the design and application of such materials in energy storage devices.
McGrier and co-workers reported benzobisoxazole-linked COFs by using cyanide as a catalyst. **COF-78** and **COF-79** were successfully synthesized utilizing C3-symmetric formyl and C2-symmetric o-aminophenol-substituted molecular building blocks (Figure 22).[77] These COFs exhibit exceptional water stability, high surface area, and remarkable CO$_2$ absorption capacity. Wang and co-workers synthesized highly crystalline benzobisoxazole-linked COFs (**COF-79** to **81**) by employing N-methyl-2-pyrrolidone/resorcinol as a solvent mixture with benzoxazole as an additive (Figure 22).[78] These COFs display excellent stability in the presence of acids, bases, and sunlight. In addition, the incorporation of the benzothiazole moiety in the π-conjugated COF framework diminishes the optical band gap and enhances the visible light absorption capacity. Benefiting from the reinforced covalent linkage in its structure, **COF-79** exhibits excellent recoverability, and its activity and crystallinity remain unaffected even after 20 runs.
Dong and co-workers have employed a natural-sunlight-mediated photocatalytic polymerization technique for the synthesis of COFs.\[^{79}\] By employing TBA-eosin Y as an assistant, the reaction of 2,5-diamino-1,4-benzenediolic dihydrochloride with 1,3,5-tris(4-formylphenyl)triazine resulted in the facile production of benzoxazole-linked COF COF-81 in satisfactory yield via solar photocatalytic synthesis (Figure 22). This eco-friendly approach, which is triggered by clean energy, enables the COF synthesis to be more sustainable than the conventional solvothermal synthesis of COF-81, which involves high temperature, high pressure, and stoichiometric amounts of additives. The resulting COF-81 can serve as a reusable photocatalyst that efficiently promotes the visible-light-driven oxidation of sulfides to sulfoxides under mild conditions.

Back and co-workers reported the transformation of reversible COF-82 to irreversible COF-83 via post-oxidative cyclization (Figure 23).\[^{80}\] 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was chosen as the oxidizing agent, which not only promotes the reaction directly but can also be easily removed after the completion of the reaction. This post-oxidative cyclization strategy has yielded COF-83 with high crystallinity and porosity. The resulting COF-83 exhibits superior thermal and chemical stability compared to COF-82 due to the stable and rigid benzoxazole linkage.

The same group further produced COF-84, which possessed a densely aromatic structure (Figure 23).\[^{81}\] The resultant COF-84 displayed both crystallinity and porosity. Partial carbonization occurred in the grain boundaries of the COF-84 subsequent to heat treatment (COF-84-600°C). This treatment led to improved electrical conductivity. Notably, the immobilization of platinum single atoms onto the nitrogen sites within the pores of COF-84-600°C resulted in superior electrocatalytic properties for the acidic hydrogen evolution reaction.

5. Dioxin Linkages

In 2019, Yaghi and co-workers reported a novel class of COFs referred to as dioxin-linked COFs, namely COF-86 and COF-87 (Figure 24).\[^{82}\] In contrast to the typical reversible condensation reactions employed in most COF synthesis, irreversible nucleophilic aromatic substitution reactions were utilized. This unique strategy resulted in these COFs with exceptional chemical stability in both acidic and basic environments. COF-86 can be post-modified by concentrated sodium hydroxide solution and hydroxylamine, resulting
in the production of COF-88 and COF-89. Notably, the crystallinity of both COFs remained intact following post-modification. Because these reactions are irreversible, the resultant frameworks have high chemical stability in both acid and base.

Qiu and co-workers reported the synthesis of polyarylether-based COFs (COF-85, COF-86, COF-90 and COF-91) via nucleophilic aromatic substitution reactions between o-difluorobenzene and catechol (Figure 24). The resulting materials exhibited remarkable chemical stability in boiling water, strong acids, and bases, as well as oxidizing and reducing conditions. Moreover, these polyarylether-based COFs can be post-synthetically functionalized with carboxyl or amino groups, keeping porosity, high stability, and recyclability. Such features make these materials promising candidates for various applications, including the removal of antibiotics from water across a broad range of pH values.

![Figure 24. The synthesis and structures of COF-85 to COF-91](image-url)
Figure 25. The synthesis and structures of COF-92 to COF-96

6. β-Amino Enone Linkages

Perepichka and co-workers reported β-amino enone-linked COFs (COF-92 to 95) through dynamic condensation of Michael addition-elimination reactions between β-ketones and aromatic amines (Figure 25). The obtained COFs exhibit better hydrolytic stability and more efficient π-electron delocalization. The emission of fluorescent COF-94 and COF-95 can be effectively quenched in the presence of nitroaromatic (picric acid) and peroxide explosives. This synthetic strategy paves the way for the development of electronically functional COFs and their potential applications in semiconductors and sensing devices.

Bojdys and co-workers reported a 2D COF (COF-96) condensed from the C2-symmetric keto-enol and the C3-symmetric triamine (Figure 25). COF-96 was found to be capable of real-time, reversible optical and electronic sensing of volatile acids and bases. The optical and electronic activity of the COF-96 was achieved through preferential protonation of triazine nitrogen, leading to two-orders of magnitude increase in optical response and bulk conductivity that was visible to the naked eye. The single-point protonation triggered the entry of π electrons into the triazine ring, accompanied by a fluorescence burst. Both optical and electronic effects involved the entire π-aromatic skeleton. COF-96 was not only chemically stable to the corrosive trigger molecule but also permanently porous to the chemisorbed guest.

7. Post-Synthetic Modification

The synthesis of fully conjugated COFs with enhanced chemical stability and optoelectronic properties can be achieved through post-synthetic modification. In this approach, Imine-linked COFs are converted into ultra-stable porous aromatic frameworks. For instance, Lotsch and co-workers have reported the topochemical
conversion of triphenyl triazine-based Imine-linked COFs (COF-99) into thiazole-linked COFs (COF-100) through a post-synthesis locking strategy involving elemental sulfur (Figure 26).[86] This method leads to a change in the symmetry of the COF crystals while maintaining their original topology, thereby improving their chemical stability. Similarly, Liu and co-workers have converted dynamic imine linkages into a more stable quinoline aromatic ring system via the za-Diels-Alder cycloaddition reaction, obtaining quinoline-linked COFs (COF-98) with significantly enhanced chemical stability (Figure 26).[87]

Yaghi and co-workers exhibited that the imine-linked COFs (COF-101) can be transformed into two distinct heterogeneous COFs, namely COF-102 and COF-103, featuring thiazole and oxazole linkages, respectively (Figure 26).[88] This conversion was achieved through successive substitution and oxidative cyclization procedures. These materials exhibit higher chemical stability compared to their amine-substituted starting materials.

Zhao and co-workers reported the synthesis of two ultra-stable fully conjugated two-dimensional COFs (COF-105 and COF-107) linked by thieno[3,2-c]pyridine units using post-oxidative cyclization (Figure 27).[89] The dynamic imine bond and the adjacent thiophene can be converted to thieno[3,2-c]pyridine by oxidative cyclization. Thieno[3,2-c]pyridines have not been previously used as linkages for COFs construction. The resulting COFs exhibit superstability and good electron delocalization. Notably, the small structural differences can lead to completely different photocatalytic activities. The fully π-conjugated COF-107 with a triazine core showed an excellent photocatalytic NADH regeneration rate of 74% within 10 min. Overall, these post-synthetic modification strategies offer a powerful approach to enhance the chemical stabilities and optoelectronic activities of COFs, opening new avenues for their applications in various fields.
Figure 26. The synthesis and structures of COF-97 to COF-103
Wang and co-workers reported a novel methodology for the synthesis of robust COFs (COF-108 to COF-111) through multicomponent reactions (Figure 28). By inducing the formation of five covalent bonds within each cyclic imidazole ring in situ, a series of imidazole-linked COFs was fabricated in a robust manner from three readily available components via the Debus-Radziszewski multicomponent reaction. This study opens up a new avenue for the precise covalent assembly of crystalline COFs.

Dong and co-workers developed a strategy for the synthesis of COFs through multicomponent one-pot in situ reactions. Specifically, they obtained a series of $\alpha$-aminonitrile and quinoline-linked COFs (COF-112, 113, 115 to COF-124) by employing a three-component one-pot in situ Strecker and Povarov reaction under solvent-heated conditions (Figure 29). The obtained COFs exhibited high crystallinity and permanent porosity. Compared to the stepwise post-synthetic modification methods, the multicomponent approach offers several advantages, including increased efficiency and versatility.
one-pot synthetic strategy can avoid the collapse of the frameworks and maintain crystallinity. This work presents a novel synthetic method that guarantees high yields while maintaining high crystallinity and porosity.

Cooper and co-workers reported a simple and efficient three-component assembly reaction between readily available aldehydes, amines and elemental sulfur via C-H functionalization and oxidative cyclization under transition-metal-free conditions. This one-pot method successfully prepared five highly stable thiazole-linked COFs (COF-125 to COF-129) through a range of functionalized aldehydes and amines (Figure 30). Among these COFs, COF-129 exhibits high photocatalytic activity toward hydrogen evolution from water. A maximum rate of 4296 μmol h⁻¹ g⁻¹ under visible light irradiation was achieved, as well as high recoverability for 50 hours of continuous hydrogen evolution.

9. Conclusions and Perspectives

Fully conjugated COFs have emerged as a significant development in the field of COFs since their successful preparation. This review provides a comprehensive overview of recent developments in the structure, synthesis, and applications of fully conjugated COFs, which possess outstanding chemical stability, continuous π-conjugation, and high crystallinity. These properties have led to the application of fully conjugated COFs in a diverse range of fields, including LIBs, photocatalytic hydrogen production, supercapacitors, and multiphase catalysis. However, despite the impressive fully conjugated COFs face a number of challenges that must be overcome.

Figure 29. The synthesis and structures of COF-112 to COF-124
Figure 30. The synthesis and structures of COF-125 to COF-127

One of the most important issues is the lack of a deep understanding of the growth and nucleation processes of fully conjugated COFs, which limits researchers to the predictive synthesis and rational upgrading of fully conjugated COFs. Single-crystal preparation of fully conjugated COFs is currently needed because a high degree of structural integrity is essential to elucidate the nature and origin of fully conjugated COFs. In addition, how to translate the structural designability of fully conjugated COFs into the designability of properties is worthy of deeper investigation. Clarifying the correlation between structure and performance will greatly expand the application area of fully conjugated COFs. A deeper investigation of the correlation between the structure and performance of fully conjugated COFs is necessary to expand their application areas. Moreover, the limited range of applications of fully conjugated COFs, primarily in photocatalysis, calls for urgent expansion. In contrast, other types of COFs, such as imine-linked COFs, are widely used in gas separation, sensing, seawater desalination, chiral chemistry and sensing, among others. Advancements in the application of fully conjugated COFs will promote their further development.

Additionally, the huge trial and error work in the synthesis of fully conjugated COFs hinders its development and applications. Therefore, the development of more widely applicable synthesis methods through innovation in monomers, catalysts and other factors is crucial to accelerate the synthesis of fully conjugated COFs. Finally, fully conjugated COFs are still in their infancy and require more scientific effort. Only a few 3D COFs have been reported successfully thus far, necessitating the development of more diverse synthesis methods and structures to expand the library of 3D fully conjugated COFs and support their further development in the future. Despite these challenges, the unique structure and excellent properties of fully conjugated COFs position them at the forefront of COFs. We envision that the combination of post-synthetic modification and multicomponent one-pot reaction will further diversify the portfolio of fully conjugated COFs in an easier way.
Innovations in energy sources, monomer design, catalysts, nucleation control, and workup activation, as well as computational high-throughput screening, can accelerate the discovery process of fully conjugated COFs. Furthermore, the integration of fully conjugated COFs with functional materials such as metal nanoparticles, enzymes, MOFs, and polymers can lead to the development of fully conjugated COFs-based composites, which is still in its nascent stage and merits more scientific efforts. Lastly, a mechanistic understanding of the formation and performance of fully conjugated COFs in specialty applications is of paramount importance for their mechanism-based synthesis and rational improvement. Although fully conjugated COFs are still in a nascent stage, continuous and interdisciplinary scientific endeavors along these promising directions will lay a solid groundwork for their bright future.

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