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Toward High-crystalline Covalent Organic Framework *via* Dynamic Condensation of Carbon-Carbon Double Bond

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Abstract Dynamic covalent chemistry (DCC) is a type of reversible chemical reactions under the control of thermodynamics. The reversibility of DCC allows the exchange of reaction components to form thermodynamically stable products. This kind of reaction has been widely incorporated in various research directions, holding an important significance in guiding emerging fields, such as two-dimensional macrocycles, two-dimensional materials and three-dimensional molecular cages. Of them, covalent organic frameworks (COFs), as a class of high crystalline porous conjugated polymers linked by dynamic covalent bonds exhibit huge potential application in various fields, such as gas separation, catalysis, sensing, biomedicines, and electronic devices due to their long-range ordered structures, regular pore distribution, high specific surface areas, and excellent molecular material designability. Vinylene-linked COFs feature high chemical stability and outstanding π-electron delocalization, extremely desired for the development of high-performance semiconducting catalysts and device. However, given that the formation reaction of carbon-carbon double bond only exhibited much poorer reversibility than those of the traditional dynamic covalent bonds, it still a big challenge to well-control the preparation of high-quality vinylene-linked COFs. In this review article, we intend to summarize the synthetic strategy approach to 2D vinylene-linked COFs on the basis of the rational design of the key monomers and the optimized reaction conditions for efficiently promoting Knoevenagel/aldol condensation. Then, we exemplified several applications arising from the unique characters of such kinds of COFs. Eventually, the challenges and opportunities of vinylene-linked COFs were also foreseen.

Keywords Covalent organic frameworks; Vinylene linkage; Dynamic condensation; Monomer design; Semiconducting properties

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1 INTRODUCTION

Covalent organic frameworks (COFs), as a new type of conjugated polymers, have attracted increasing attentions and in-depth explorations from researchers worldwide in recent years. As a class of high crystalline porous conjugated polymers linked by dynamic covalent bonds, COFs have been widely applied in various fields, such as gas separation, catalysis, sensing, biomedicines, and electronic devices due to their long-range ordered structures, regular pore distribution, high specific surface areas, and excellent molecular material designability. Since Yaghi *et al*. synthesized the first COFs through boronic acid ester condensation reaction in 2005,[1] this field has undergone two decades of rapid development with researches in all its aspects becoming matured. Currently, the researches mainly focus on the following areas: (1) synthesizing monomers with reactive groups to expand new structures; (2) increasing the functionality of monomers to prepare frameworks with complex topology; (3) exploring new bonding reactions to enhance the reversibility and self-healing ability of dynamic covalent bonds; (4) developing new preparation methods to enhance the universality of material synthesis and reduce reaction costs; (5) searching for new application scenarios; (6) post-modifying the synthesized materials to expand application ranges; and (7)

compositing with other materials to improve performance, *etc.*

2 DYNAMIC COVALENT CHEMISTRY AND LINKAGE

Dynamic covalent chemistry (DCC) is a type of reversible chemical reactions under the control of thermodynamics. The reversibility of DCC allows for the exchange of reaction components to form thermodynamically stable products.[2,3] Currently, this kind of reactions has been widely incorporated in various research directions, which not only holds important significance in guiding the emerging fields, such as two-dimensional macrocycles, two-dimensional materials and three-dimensional molecular cages, but also has huge application potential in many areas including drug development, biotechnology usage, molecule separation and light capture. DCC mainly relies on the reversible formation and cleavage of intramolecular covalent bonds which are fairly strong. Therefore, it combines the error-correction ability of supramolecular chemistry (SC) and the stability of covalent bonds.

The remarkable feature of DCC is the dynamic process, which allows the exchange of reaction components at equilibrium state to achieve the thermodynamic minimum of the system. Due to the above characteristic adaptiveness on system equilibrium, the main application of DCC is to develop stimuli-responsive dynamic functional materials, which play a key role in novel technologies such as self-healing systems, sensors and actuators. While compared with SC, which utilizes weak non-covalent interactions such as hydrogen bonds or coordination bonds, the speeds of formation and dissociation of chemical bonds in DCC are usually slow. For reversible covalent reactions applicable to DCC, several factors must be considered. (1) Lifetime of covalent bond. Generally, the lifetime of the reversible bond should be within the range of 1 ms < τ < 1 min to ensure that these covalent bonds are stable enough to maintain the detectability and separability of molecular structures, while still having dynamic behaviors.[4] (2) Reaction conditions. It requires mild reaction conditions compatible with the extensive reactive groups present in building blocks and units. (3) The exchange process should be easily stopped to isolate the target products.

Dynamic covalent chemistry has two types of reactions: one is an exchange reaction involving the transformation of one reaction building block into another, thereby forming a product with the same bonding type; the other is the formation of new dynamic covalent bonds, including condensation and addition reactions.[5] Dynamic covalent bonds include C—C bond, C—N bond, C—O bond, C—S bond, S—S bond and B—O bond, *etc.* The C—C bond, as a representative of the above bonds, has been widely used in the synthesis of complex molecules and polymers (Fig. 1). The formation of C—C bond generally depends on appropriate catalysts, solvents, temperatures and other reaction conditions to enhance the reversibility of the bonding reaction. In the meanwhile, the B—O bond is usually formed by the self-condensation of boronic acids or the condensation with diols, which can be reversible under certain conditions.[6] The imine bond is formed by the reversible condensation between an amine

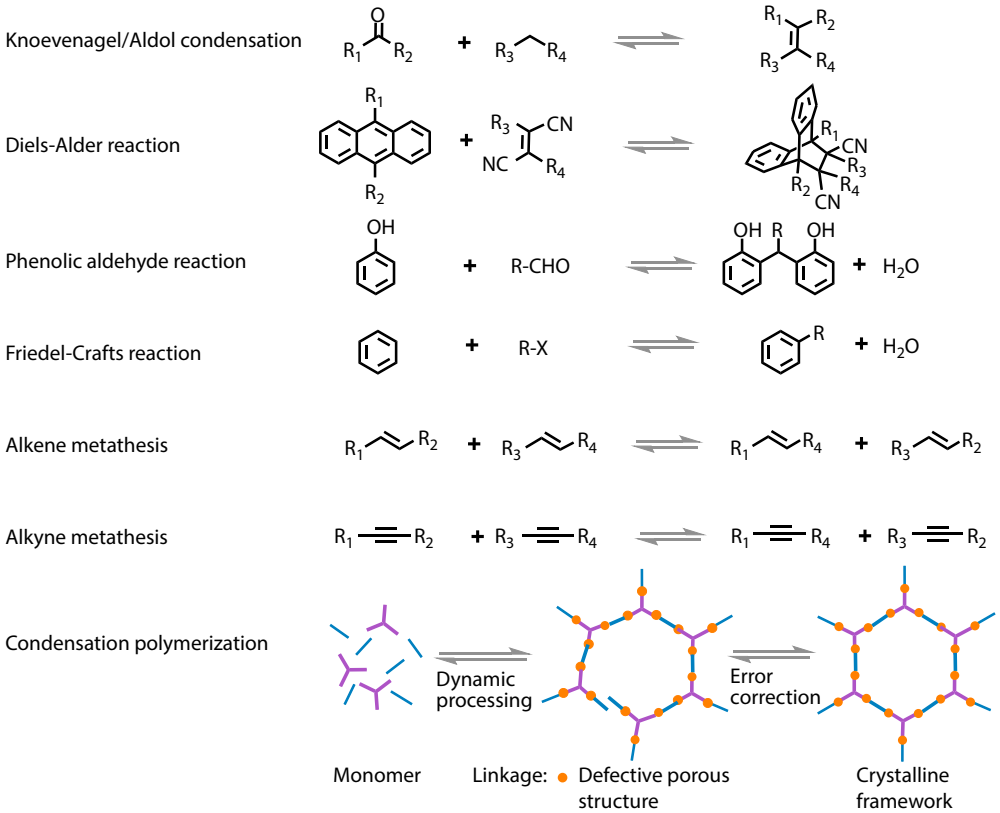

Fig. 1 Chemical reactions can be used to form dynamic carbon-carbon bonds.

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and an aldehyde. This reaction is one of the common reactions in organic chemistry.[7]

Knoevenagel condensation is a type of aldol condensation, supposed to experience two main steps. (1) Formation of an aldol intermediate by nucleophilic addition of an active methylene compound to a carbonyl group of either aldehyde or ketone; (2) Generation of carbon-carbon double bond by elimination of one molecule of water from the formed aldol intermediate. In the first step, a methylene compound is typically activated *via in situ* protonated tautomers using acid catalyst, while a carbon cation of methylene compound is formed upon base catalysis.[8,9] Due to the high bond energy, low polarity and good symmetry, the C—C double bond has been regarded as an irreversible reaction for a long time. However, the recent research results indicate that the reversibility of the bonding reaction can be enhanced after changing the reaction conditions, which enables the dynamic synthesis of such bonding products. Lehn *et al*. conducted a rapid and reversible dynamic covalent C=C/C=N exchange between Knoevenagel compounds derived from 1,3-dimethyl barbituric acid and imines in non-polar solvents without any catalyst.[10] The successful synthesis of the intermediates confirmed that the conversion of the two dynamic bonds started from the nucleophilic attack of the imine nitrogen on the highly polarized C=C of the Knoevenagel compound, then formed tetra-nitrogen heterocyclic butane intermediates, and finally resulted in new imine and double bond products through ring-opening reactions. To date, dynamic Knoevenagel/aldol condensation has become one of the most powerful tools for building up high-crystalline vinylene-linked COFs, dominantly because its reversible character enables error correction to promote the formation of long range-ordered structures (Fig. 1). However, these reactions are still less controllable for the construction of crystalline frameworks in comparison with those traditional dynamic condensation reactions.[11–14]

In 2020, Zhang *et al*. verified the dynamic reversibility of the Knoevenagel condensation process of benzaldehyde with 2,4,6-tricyanomethyl-1,3,5-trimethylbenzene under the catalysis of dimethylamine.[15] This reaction could be achieved through the imine cation intermediate formed by the aromatic aldehyde and dimethylamine. Due to the appropriate electrophilicity of the cation intermediate, it could smoothly undergo addition reaction with the deprotonated monomer, resulting in the formation of the addition compounds and ultimately forming the vinylene bond through elimination process. In 2024, Perepichka *et al*. found that the methyl groups at the *ortho*-position of the carbocations in the hexamethoxytritylium (HMT) and trioxatriangulene (TOTA) could exhibit strong acidity, and their deprotonation would lead to the activation of the vinylene bond, forming the nucleophilic intermediates in Knoevenagel condensation.[16] Based on the double bond formation mechanism in the above, they explored the dynamic reversibility of this process. Through mixing the two monomers with the corresponding model compounds and catalyzing them with sodium acetate and alkali, finally the single-substituted and double-substituted products were obtained, respectively.

In 2021, Hecht *et al*. realized the dynamic covalent exchange between *α*-cyanostyrene and benzyl nitrile derivatives under the catalysis of base through dynamic Knoevenagel condensation reaction.[17] This exchange was initiated by the deprotonation of the benzyl nitrile, providing active nucleophilic reagent which can attack the vinylene bond of the *α*-cyanostyrene, further forming Michael-type anionic adduct. This negatively charged intermediate could undergo proton transfer and subsequently re-dissociate into new *α*-cyanostyrene derivative and deprotonated benzyl nitrile. The latter remained active enough to attack another chromophore or to deprotonate another nitrile (Fig. 2).

In 2022, Feng and Hecht *et al*. investigated the dynamic process during the synthesis of the vinylene-linked COFs substituted by benzyl cyanide.[18] To demonstrate the construction of the crystal frameworks involving self-correcting processes, a series of control experiments were carried out, proving that the formation of the vinylene-linkage required

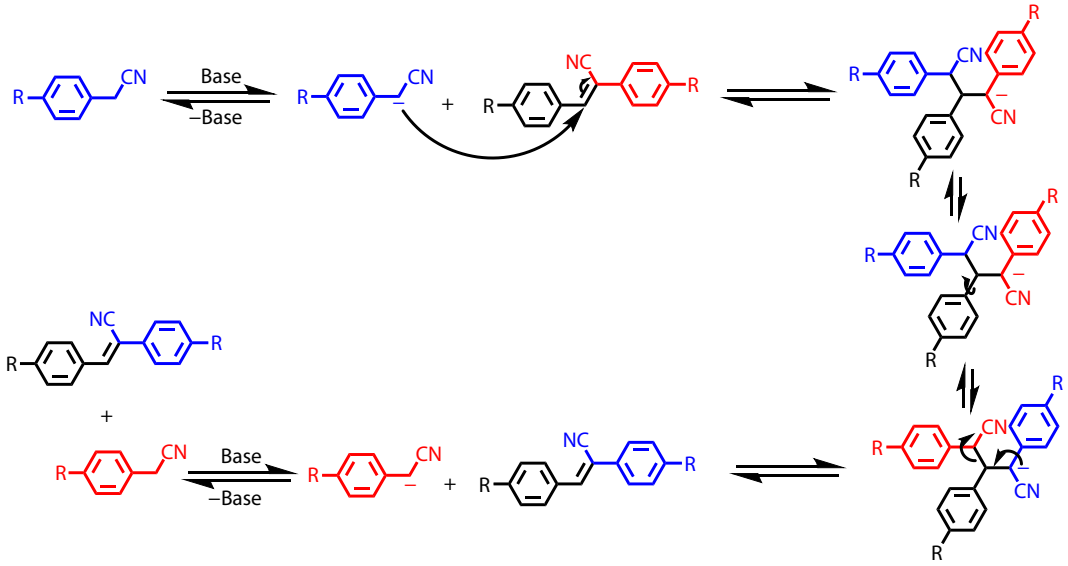

Fig. 2 Base-catalyzed dynamic covalent exchange of an *α*-cyanostilbene with a phenylacetonitrile and the proposed mechanism.

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Michael addition and subsequent elimination reaction. And the process was discussed in details (Fig. 3). Under the catalysis of cesium carbonate, HCO_3^- and CO_3^{2-} could act as donor and acceptor of proton transfer. Due to the relatively limited number of protons, Michael addition and elimination occurred at a slow rate. Hereby, they hypothesized that the above reactions of C=C bond exchange could be accelerated by adding a small amount of water, which would generate enough H_2O/OH^- as proton donor-acceptor pair to replace HCO_3^-/CO_3^{2-}. And the rationality of the proposed mechanism was verified by theoretical calculations.

Topology is a branch of mathematics and it is a powerful theoretical guidance and also an analytical tool for understanding the fundamental properties of space.[19] Compared to traditional stacking models, COFs contain a large number of channels and pores in their structures, increasing their structural complexity. For such kind of complicated network entities, topology can be used to simplify their skeletons into basic forms. Without being constrained by the feasibility of the chemical reactions between different building blocks, and only focusing on vertices and edges, it provides a clear and effective way to understand these complicated network structures.

The significance of topology in guidance on COFs is mainly reflected in the following aspects. (1) Physical property regulation: the topological structure of COFs aligns with the arrangement of pores and channels, which significantly affects their physical properties, such as specific surface areas, pore sizes and pore volumes. And these characteristics are very important in gas storage, separation and catalysis. (2) Chemical stability and reactivity: the geometric shape and connectivity of structural units in COFs can affect their chemical stability and reactivity. Some specific topological structures may produce even stable frameworks. (3) Functionalization and post-synthetic modification: the topological structures impact the accessibility of the functional groups and the ease of the function integration into COFs during the post-synthetic modification. (4) Rational design methods and optimized material synthesis conditions: topological methods can be used for the structure design of COFs effectively. (5) Structure-activity relationship: in practical applications, the verified relationships between the topological structures of COFs and their different properties can be utilized to control and predict the performance.

The structural units for COFs construction are divided into knots and linkers. Connecting different geometric shapes and symmetry knots in a 1:1 ratio forms the most common binary topological structures. In two-dimensional COFs, common ones include $[C_3+C_2]$ or $[C_3+C_3]$ connecting hexagonal frameworks, $[C_4+C_2]$ or $[C_4+C_4]$ connecting rectangular frameworks, $[C_2+C_2]$ or $[C_3+C_6]$ connecting rhombic frameworks, $[C_6+C_2]$ connecting triangular frameworks, and $[C_2+C_2]$ connecting cage frameworks. Moreover, there also exist the frameworks synthesized through multi-component strategies involving three or more building units with anisotropic irregular polygonal channels present.[20]

3 VINYLENE-LINKED COVALENT ORGANIC FRAMEWORKS

In the two-dimensional π-conjugated COFs, the conjugated framework and π-π stacking interactions between adjacent layers provide pathways for electron transfer, while the porous channels can accommodate active sites for catalysis and sensing. However, up to now, the synthesis of two-dimensional conjugated COFs still remains mainly arising from the Schiff base reaction of amine and aldehyde/ketone monomers to form imine bonds. Although this highly reversible reaction can reduce the defects and improve the crystallinity through self-healing processes, the polarization of the C=N bond also weakens the π-electron delocalization. Additionally, the poor stability in strong acidic or basic environments further limits the applications of these COFs. To improve the above shortcomings in construction of these two-dimensional conjugated COFs linked by traditional C=N bonds, researchers utilized other dynamic bond reactions to form new linkages instead, representative of vinylene linkage. Compared to other dynamic covalent bonds, C=C bond features nonpolarity and high bond energy, favorable for π-electron delocalization and stability of COFs.[21] However, traditional reactions for forming vinylene linkage have poor reversibility. The first vinylene-linked COFs were reported in 2016 by Zhang *et al.*[22] However, the available monomers for synthesizing such COFs are still rare, and the reversibility, diversity and reaction conditions of bonding formation also need further improvement. Despite the vinylene-linked COFs facing the development bottlenecks, their great potentials in many frontier fields such as catalysis, sensing, batteries and energy storage, make them become new research hotspots.

3.1 Synthesis Method of Vinylene Bond

Reactions that form the vinylene bonds are mostly carried out with specific catalyst through the condensation reaction of active methyl or methylene groups with aldehydes. To enhance the reversibility of the bond-forming reaction when preparing highly crystalline vinylene-linked COFs, currently the following condensation reactions are mainly used for construction. aldol condensation refers to the nucleophilic addition of an aldehyde or ketone with an α-H to another molecule of aldehyde or ke-

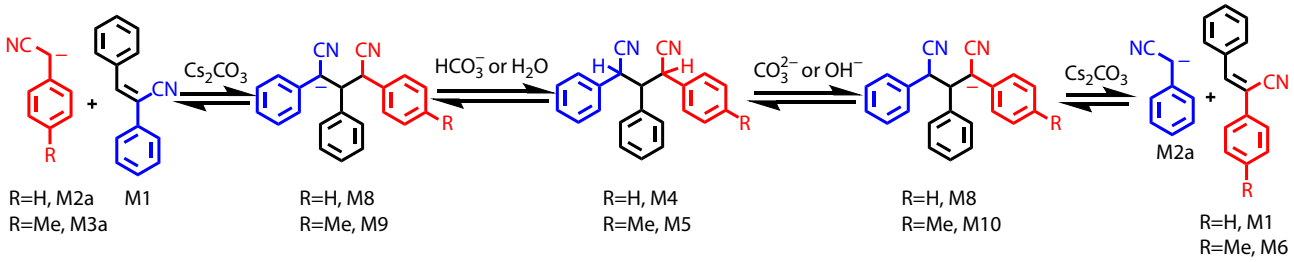

Fig. 3 The possible reaction mechanism of Michael-addition elimination.

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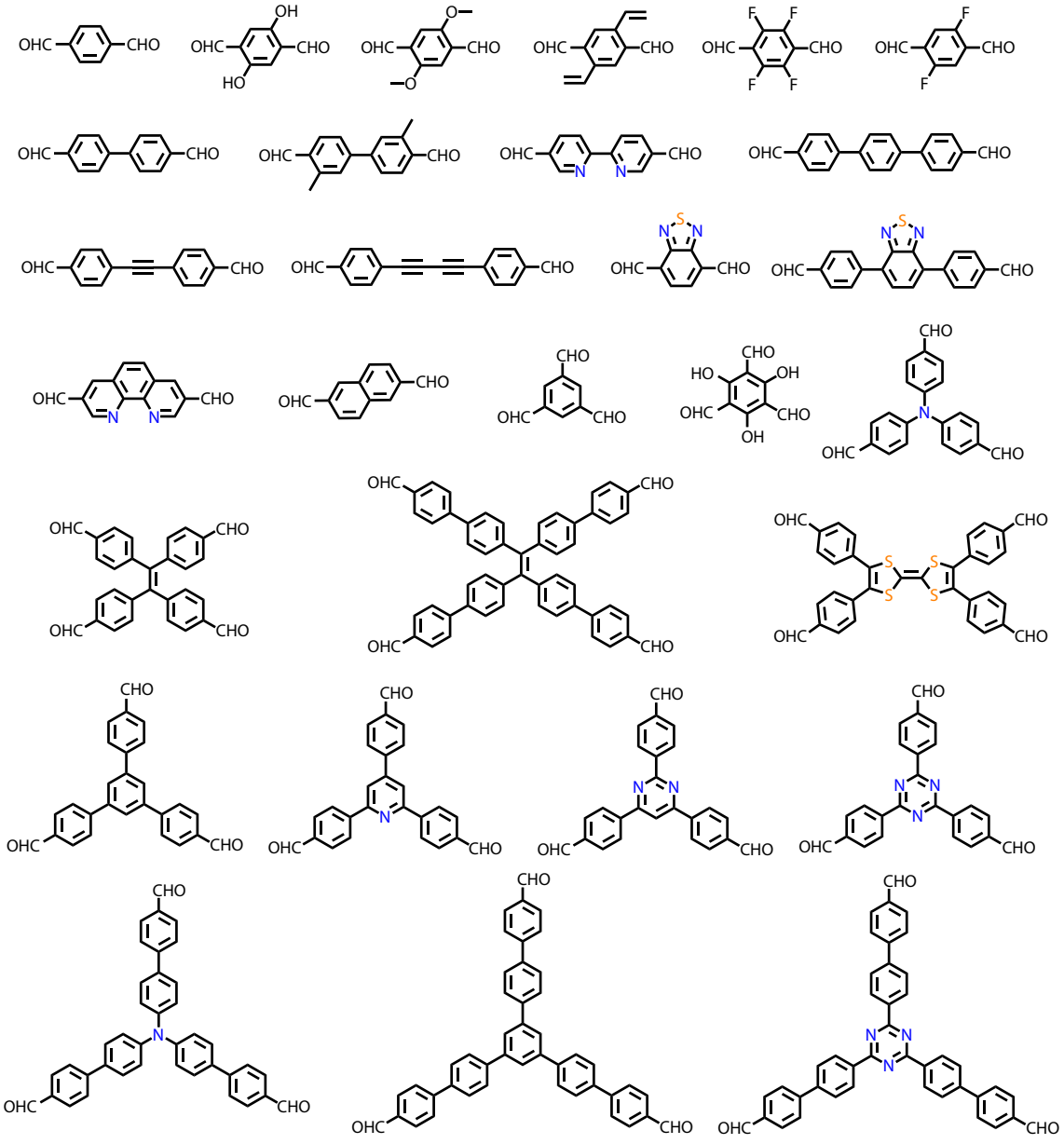
tone under acid or base catalysis, generating β-hydroxy aldehyde or β-hydroxy ketone. Knoevenagel condensation involves the nucleophilic addition of a compound with acidic CH to a carbonyl group, followed by the removal of a water molecule from the formed aldol condensation intermediate[17]. The molecules prepared through this reaction feature structural diversity and accessibility ease. More importantly, this condensation reaction is reversible under both basic and acidic conditions, thus being applicable to synthetic conditions that require high thermodynamic control.[23]

3.2 Monomers

As an important type of building units for synthesizing vinylene-linked COFs, the selection of aldehyde-based monomers is closely related to the synthesis of COFs and the quality of their crystals. By changing the types of aldehyde monomers, it enables the alteration of overall topology of COFs, the increase of active sites, the improvement of coordination effects, the regulation of optical band gaps and the enhancement of mass transfer properties. Meanwhile, the introduction of aldehyde monomers also provides a platform for other fields, such as post-modification functionalization, doping, and forming composites with other materials, which can effectively enhance the functions and properties of target COFs. Currently, the aldehyde monomers available for synthesizing vinylene-linked COFs are shown below (Figs. 4 and 5).

How to synthesize monomers with high reactivity has always been the key issue in preparing vinylene-linked COFs, as the reactivity of the α-H directly affects the considerations on various aspects, such as solvents, temperatures and catalysts during the polymerization process. It is also closely related to the reversibility of the bonding reaction, thereby influencing the crystallinity of the final product and then its application prospects (Figs. 6 and 7). Currently, the effective activation



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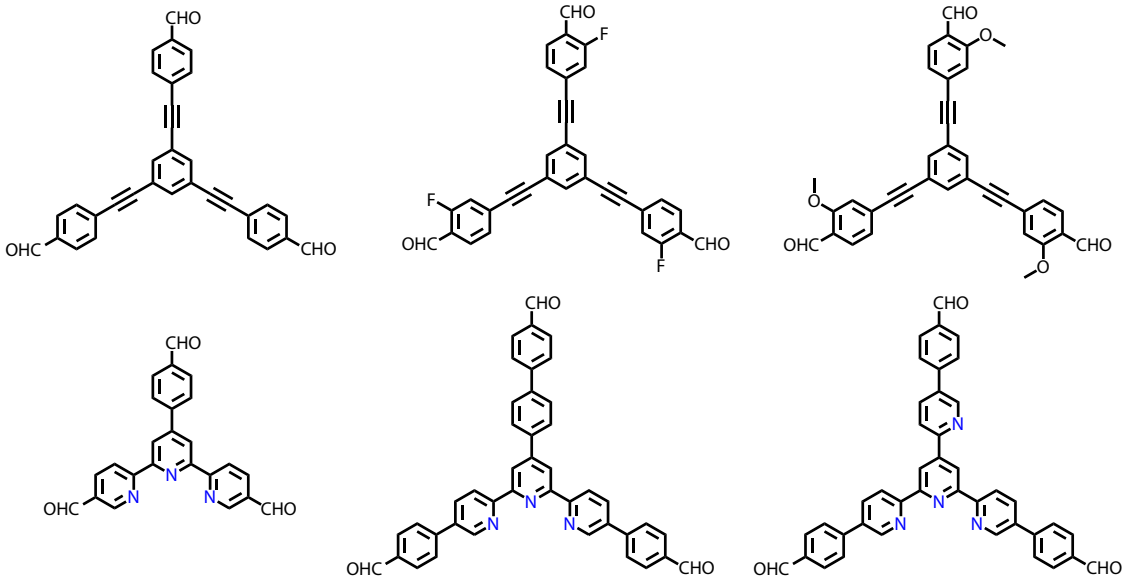

Fig. 4 Common aldehyde monomers for the preparation of vinylene-linked COFs (I).

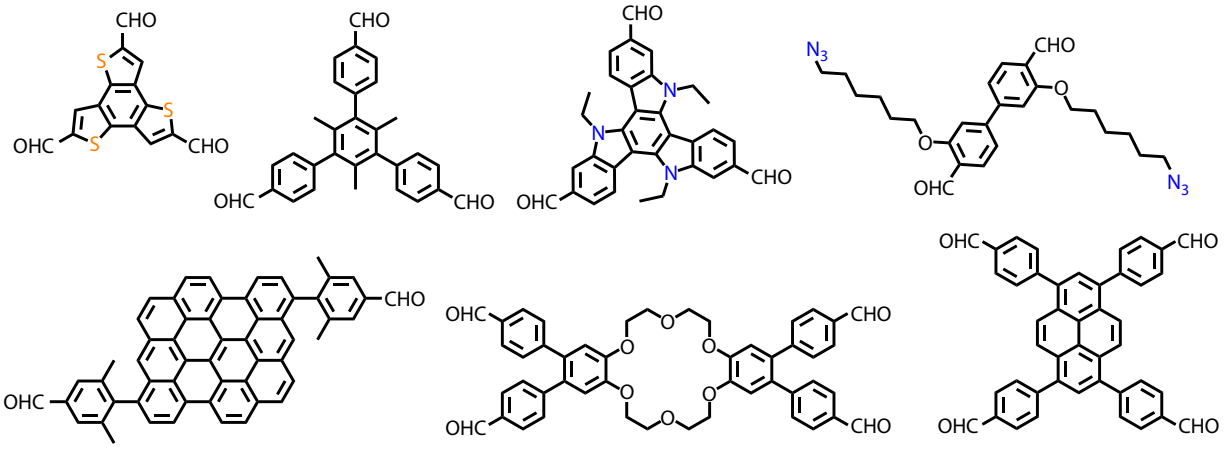

Fig. 5 Common aldehyde monomers for the preparation of vinylene-linked COFs (II).

methods, which were commonly used, mainly include the following three ones: (1) introducing electron-withdrawing groups; (2) embedding atoms with high electronegativity; (3) preparing ionic monomers. Different activation methods often correspond to different bond forming reactions. While the same reaction may also require the differences in catalytic conditions due to the various activities of the monomers. Therefore, searching for a universal synthetic catalytic strategy and summarizing the design ideas for activating monomers are of crucial significance in the future of vinylene-linked COFs development.

3.2.1 Aryl acetonitrile

As a strong electron-withdrawing group, the introduction of the cyano group can enhance the reactivity of the hydrogen atom that directly attached to the methylene group, and it can undergo condensation with aromatic aldehydes under base. Since Zhang *et al*. first reported 1,4-phenylenediacetonitrile as the core monomer for the preparation of cyano-substituted vinylene-linked COFs in 2016, thus an extensive research focusing on this type of monomers then aroused (Fig. 8).[22] In 2020, Feng *et al*. synthesized a case of cyano-substituted 2D CCP-Th with bithiophene as the node.[24] Compared to imine-linked COFs, due to its strong donor-acceptor and conjugated structure, this COFs exhibited a wide ultraviolet absorption region, a narrow band gap, a fast photoelectric response and good photocatalytic hydrogen evolution performance. The theoretical simulation confirmed that the sulfur atom in the structure and the cyano group on the vinylene bond can act as active sites for the desorption of hydrogen. In the same year, Cui *et al*. introduced a chiral aldehyde unit into the conjugated framework and reduced the C=C double bond to C−C single bond under the catalysis of sodium borohydride.[25] The complete reduction of the double bond was proved through Fourier transform infrared spectrometer (FTIR) and solid-state nuclear magnetic resonance. The reduced structure had a blue-shifted emission spectrum, high quantum yield and long fluorescence lifetime. The vinylene-linked COFs exhibited higher enantioselectivity than its reduced structures when used as a fluorescence sensor of chiral amino alcohols, thereby expanding the application of COFs in this field. To further optimize the reaction conditions, Zhao *et al*. used ammonium acetate as a catalyst to first form a

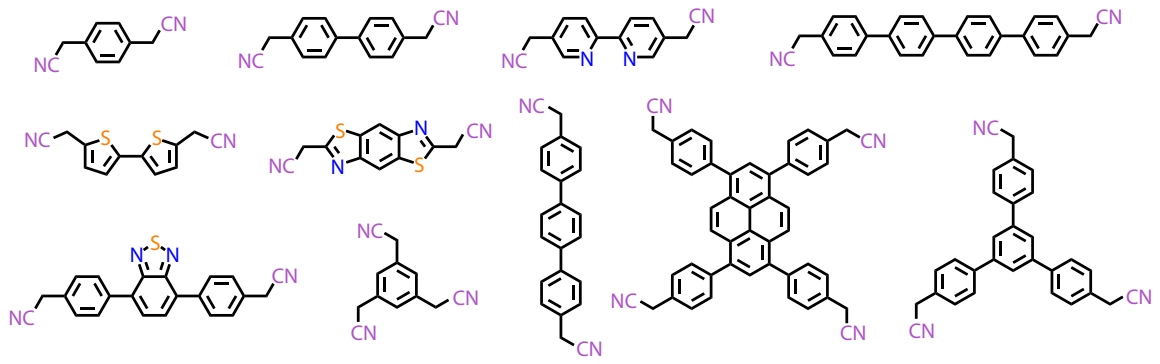

Fig. 6 Common active aryl acetonitrile monomers for the preparation of vinylene-linked COFs.

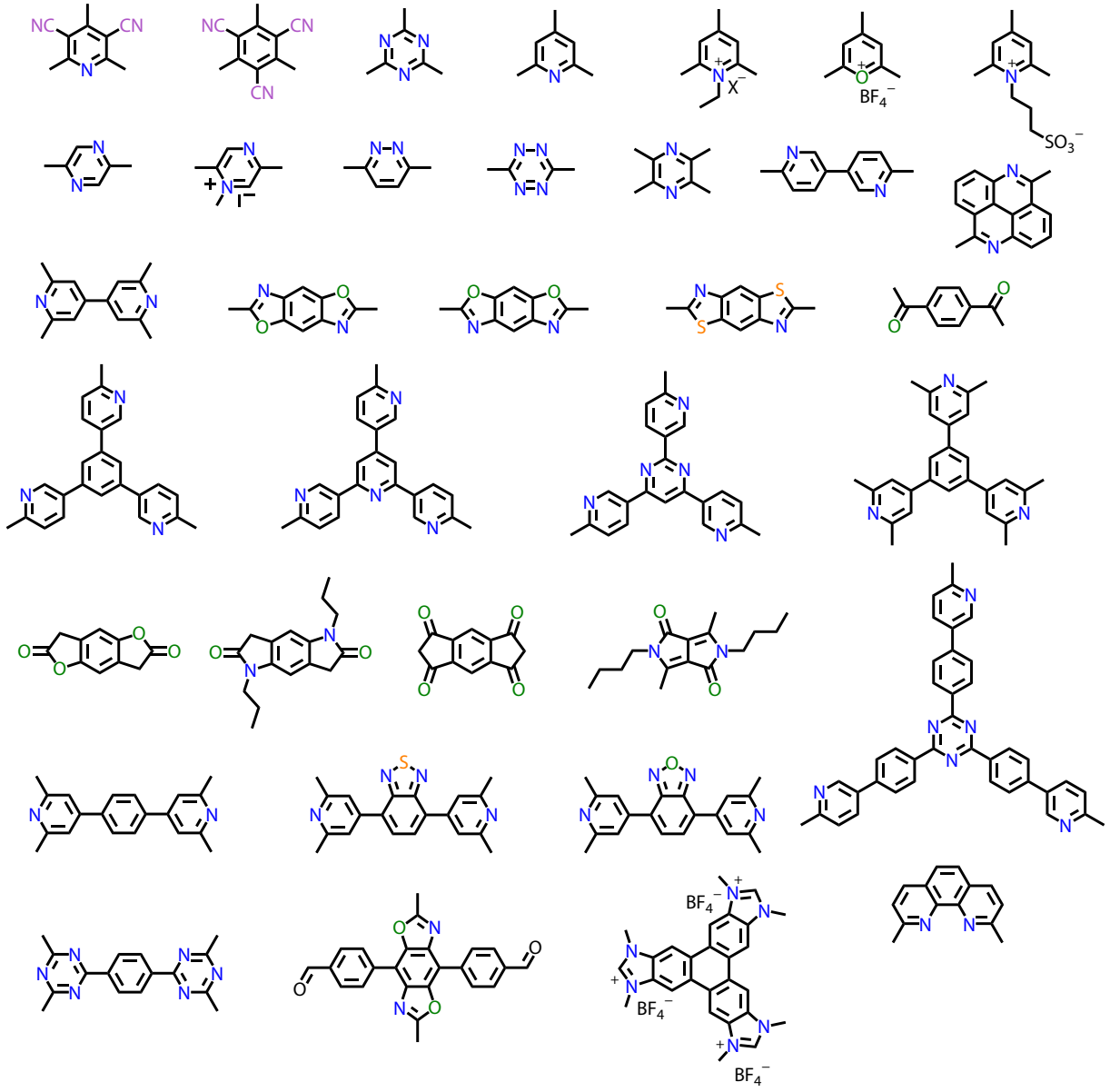

Fig. 7 Common active aryl methyl monomers for the preparation of vinylene-linked COFs.

Schiff base by condensing with the aldehydes, and then combined with a carbon anion, and then finally dehydrated to form the double bond.[26] Compared with the traditional basic catalytic environment, this method not only enhanced the reversibility of the bonding process, but also successfully prepared three vinylene-linked COFs containing benzothiazole

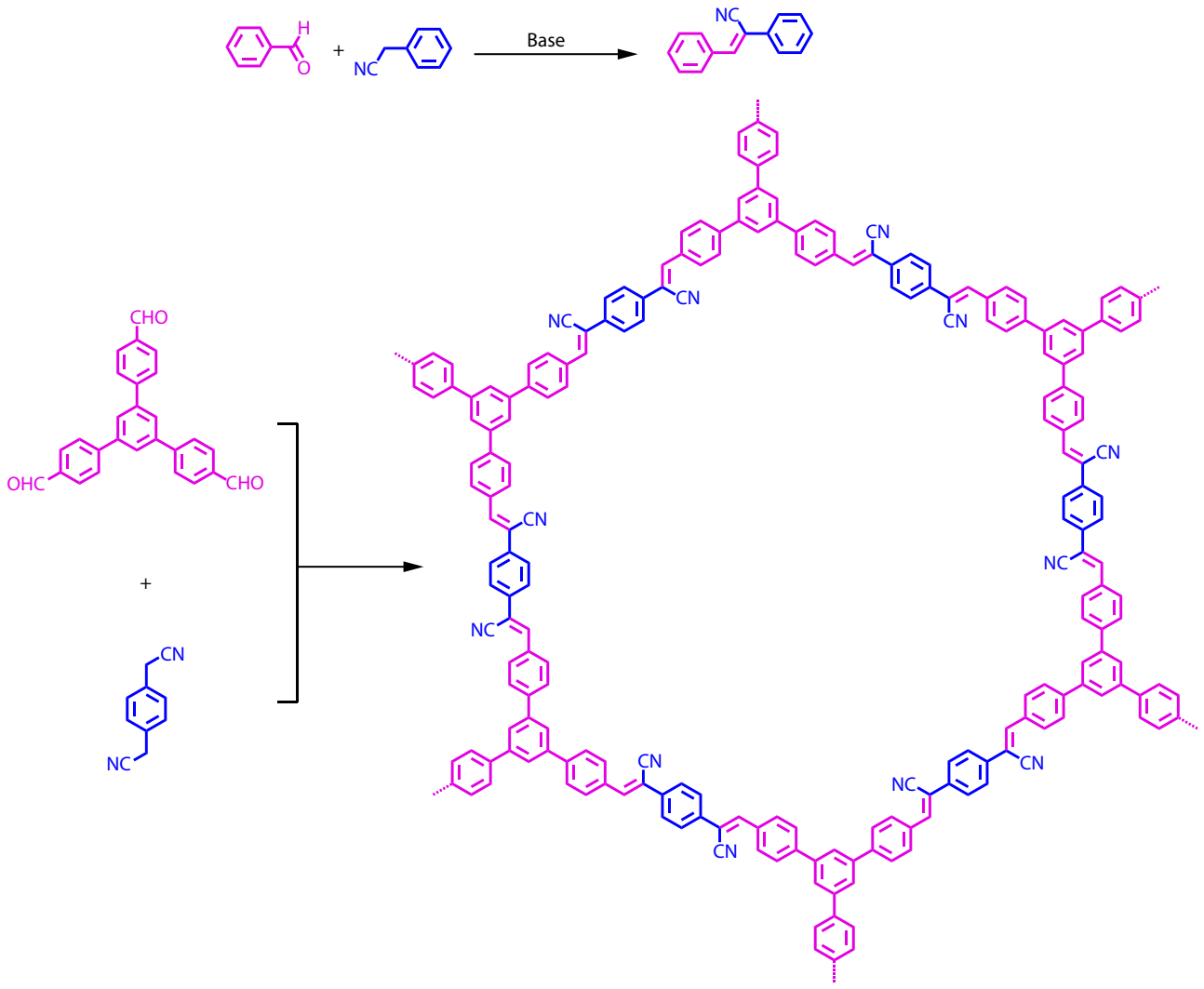

Fig. 8 Structure and synthesis of olefin-linked COFs (2DPPV).

units under relatively mild reaction conditions. In addition they achieved an excellent performance of 15.1 mmol·h^{-1}·g^{-1} in photocatalytic hydrogen production through ingeniously constructing donor-acceptor units to form an ordered D-A structure. In 2024, Xu *et al*. proved that the topological structure of a triangular lattice with high-density *π*-conjugated units was most beneficial for the charge separation and carrier migration in COFs during the light-induced process through the synthesis and comparison of three COFs with different pore shapes.[27] And it also provided a new pathway for the efficient artificial preparation of hydrogen peroxide.

3.2.2 3,5-Dicyano-2,4,6-trimethylpyridine-4

Inspired by the design concept of benzyl cyano monomers, in 2019, Zhang *et al*. developed a new monomer 3,5-dicyano-2,4,6-trimethylpyridine by directly introducing the cyano and methyl groups into the electron-deficient aromatic ring pyridine, and effectively enhancing the acidity of the methyl groups of this monomer suitable for Knoevenagel condensation.[28,29] Furthermore, they conducted the condensation of the above monomer with 4,4',4"-(1,3,5-triazine-2,4,6-triyl)tribenzaldehyde to successfully synthesize a vinylene-linked COF termed *g*-$C_{34}N_6$-COF with a fibrous morphology under the catalysis of piperidine.[30] Then, this COFs were composited with single-walled carbon nanotubes (SWCNTs) to fabricate a thin-film electrode for supercapacitor, demonstrating a surface capacitance of up to 15.2 mF·cm^{-2} and a high energy density of 7.3 mW·h·cm^{-3}, which was superior to the previously reported materials of the same type at that time. Subsequently, they further expanded the scope of the aldehyde monomers and deeply discussed the influence of the distribution of D-A structure on the structural polarity and photoelectric properties of the COFs.[31] In 2021, Müllen *et al*. prepared a polycyclic aromatic aldehyde, 6,14-bis(4-formyl-2,6-dimethylphenyl)dibenzo[*hi,st*]ovalene (DBOV), and condensed it with this methyl monomer to obtain a DBOV-COF with ABC stacking mode (Fig. 9).[32] They verified the reliability of this stacking mode by means of powder X-ray diffraction (PXRD) and transmission electron microscope (TEM) and also provided a simple strategy for introducing various functional nanographene into the frameworks. In 2023, Lan *et al*. condensed this monomer with a copper-coordinated C_3 symmetric aldehyde monomer and compared it with the reported *g*-$C_{34}N_6$-COF.[33] It proved that regulating the electron-deficient/rich

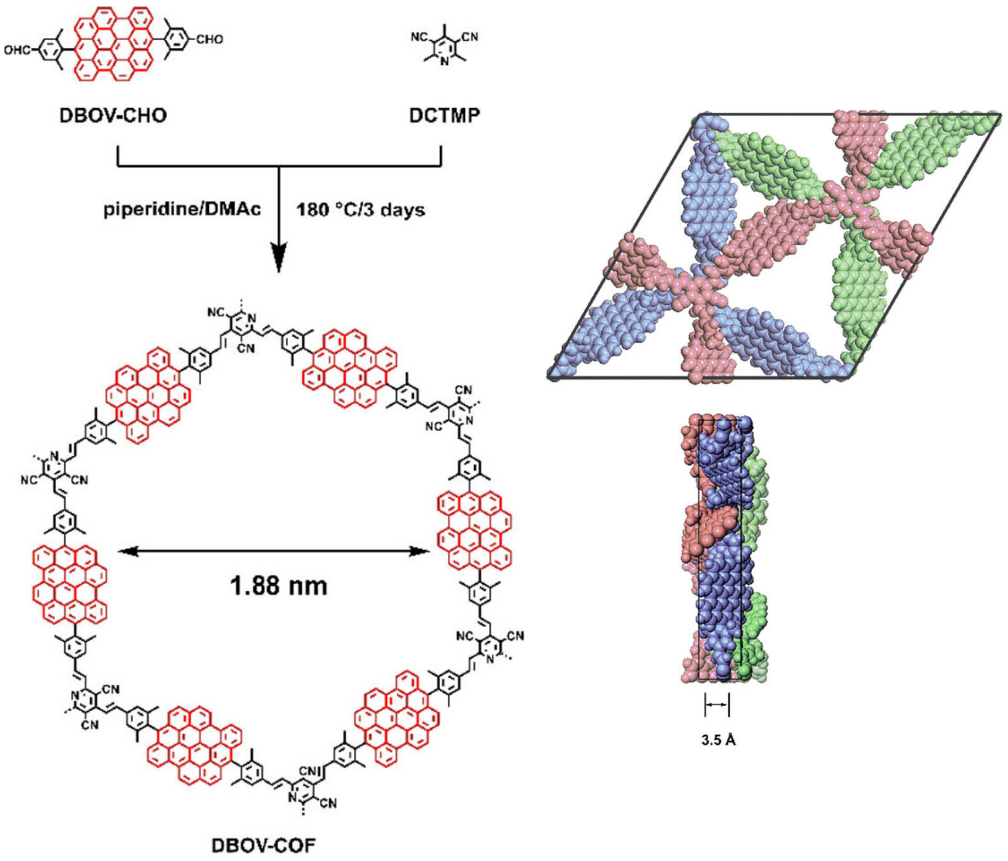

Fig. 9 Synthesis of DBOV-COF and its simulated structures with ABC stacking (Reproduced with permission from Ref. [32]; Copyright (2015), Wiley-VCH).

properties of the building units can control the charge separation rate of COFs as a catalyst and thereby can affect the photocatalytic performance of COFs.

3.2.3 Tricyanomesitylene

In 2017, Zhang *et al*. first attempted to synthesize COFs by preparing tricyanomesitylene under piperidine catalysis to further enhance the symmetry and planarity of the structure and strengthen the delocalization of π-electrons.[34] But unfortunately, the resulting structures were amorphous. Upon optimizing the condensation conditions by simultaneously activating both arylmethyl and carbonyl monomers, three highly crystalline vinylene-linked COFs were synthesized by combining tricyanomesitylene with aromatic aldehydes of various symmetries.[15] Compared with the previous polymerization conditions, and given that piperidine acted as the effective base catalyst in synthesizing amorphous product, it was proposed that this reaction might first generate an imine cation intermediate of the aldehyde group, and then react with the carbon anion of the methyl monomer, and then finally dehydrate to form the double bond, which followed the Knoevenagel condensation mechanism (Fig. 10). Furthermore, a large number of condition screenings were conducted. Using dimethylamine as the catalyst a series of highly crystalline vinylene-linked COFs were obtained finally. These COFs could efficiently convert the arylboronic acid compounds into arylphenol ones under visible light irradiation. At the same time, they also proved, through a comparison with 2,4,6-trimethylpyridine-3,5-dicarbonitrile, that the high symmetry octupole structure formed by tricyanomesitylene was even beneficial to charge separation.[30]

3.2.4 2,4,6-Trimethyl-1,3,5-triazine

The active *α*-carbon atom in 2,4,6-trimethyl-1,3,5-triazine is prone to form a carbon anion intermediate, which could further form the C=C bond. This monomer is readily available, and the vinylene-linked small molecules prepared based on it have high symmetry, good planarity and low dipole moment, which benefits to intramolecular stacking. These characteristics are beneficial for constructing vinylene-linked COFs. Yaghi *et al*. firstly reported the COFs based on this triazine core, which were obtained through the reaction with 4,4'-biphenyldicarboxaldehyde in a mixed solvent of mesitylene, 1,4-dioxane and acetonitrile under the catalysis of trifluoroacetic acid.[35] Moreover, due to the presence of the C=C bond, it also exhibited excellent chemical stability in various Brønsted acids, bases, and even organic lithium reagents. Therefore, $BF_3{\cdot}OEt_2$ was loaded on these COFs to catalyze the Diels-Alder reaction with a high yield. Subsequently, Zhang *et al*. prepared two high-crystalline COFs through Knoevenagel condensation of this monomer with 1,4-phthalaldehyde or 1,3,5-tri(4-methylphenyl)benzene, respectively, in a mixed solution of *n*-butanol and 1,2-dichlorobenzene under the catalysis of strong bases (KOH or EtONa).[36] This work further enriched these types of vinylene-linked COFs (Fig. 11). The PXRD spectra of these two COFs were in good agreement with the simulation results, and their high specific surface areas were verified by nitrogen adsorption tests. Due to their or-

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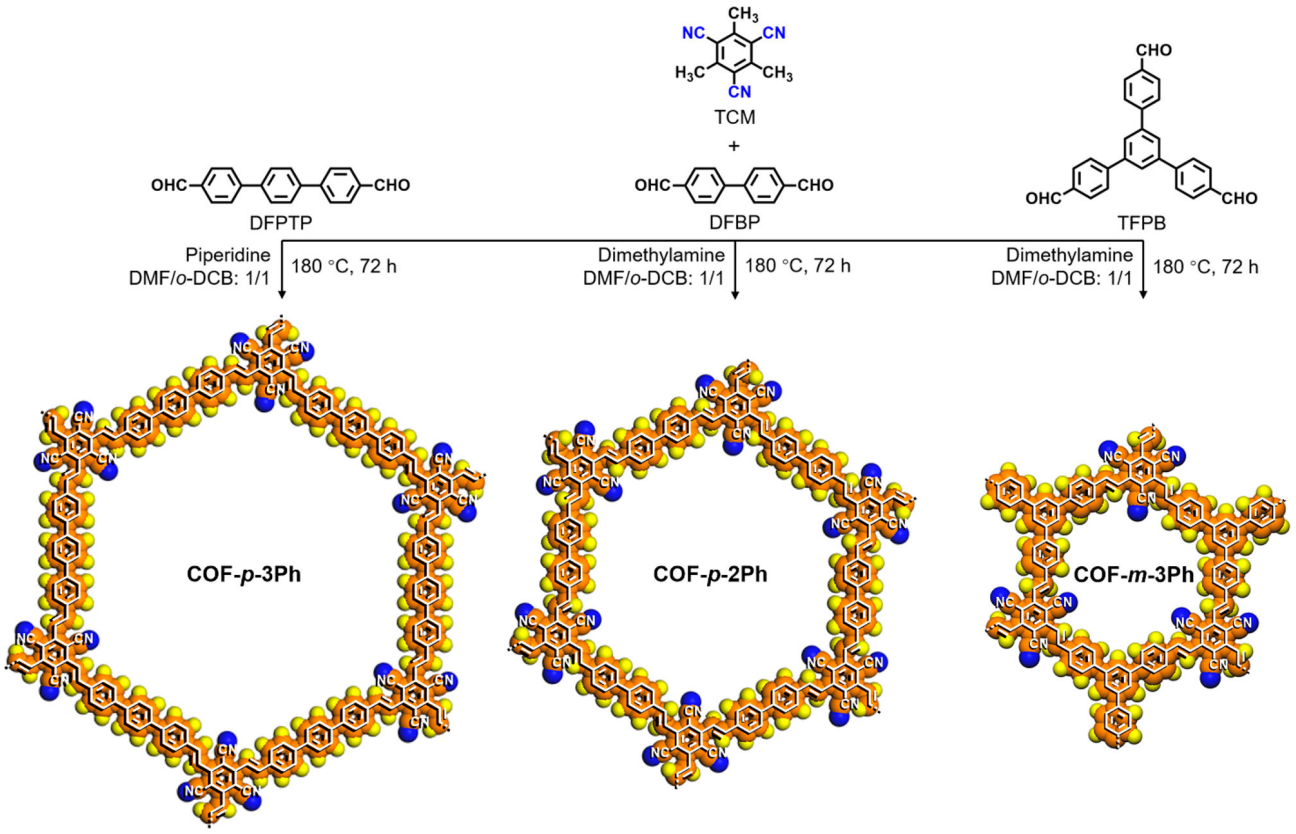

Fig. 10 Synthesis routes to COF-*p*-3Ph, COF-*p*-2Ph, and COF-*m*-3Ph (Reproduced with permission from Ref. [15]; Copyright (2020), American Chemical Society.)

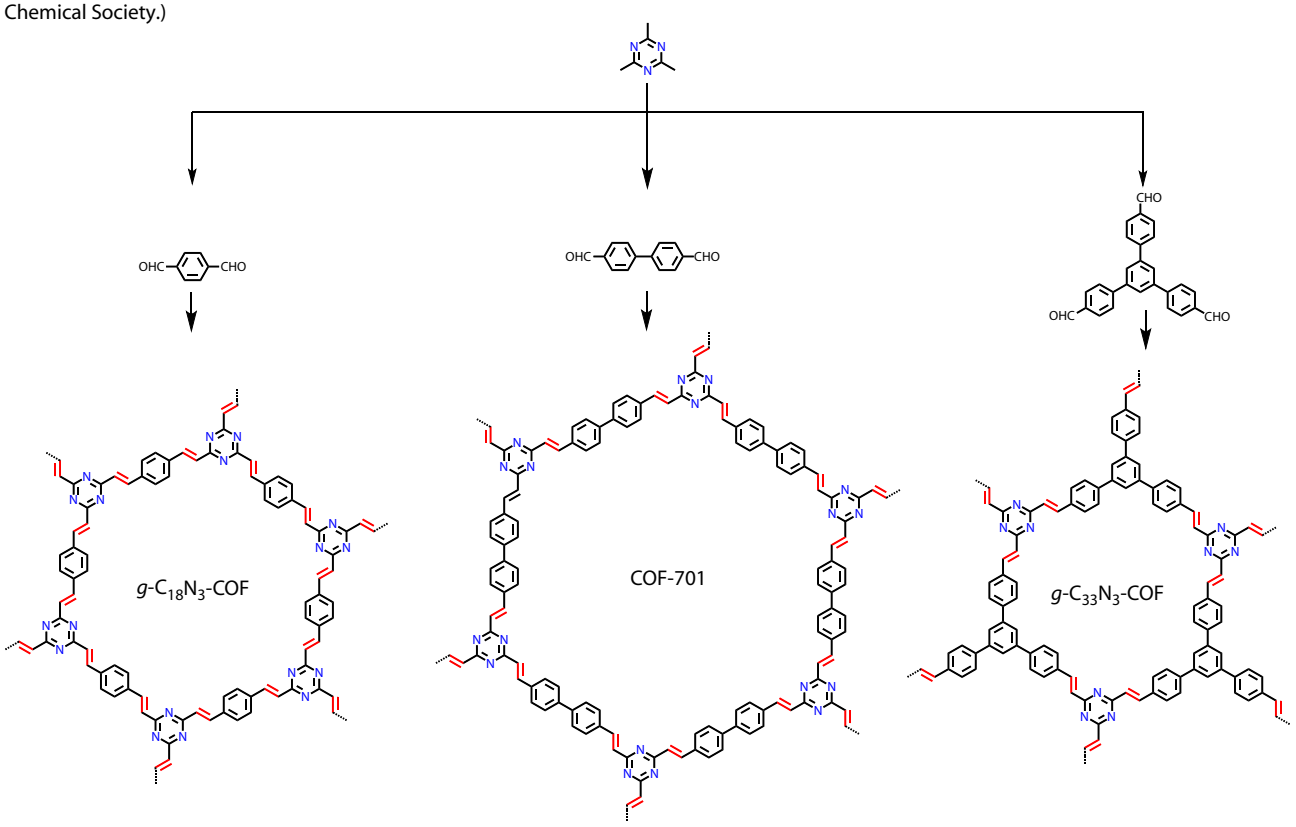

Fig. 11 Synthesis routes and structures of *g*-C18N3-COF, COF-701 and *g*-C33N3-COF (Reproduced with permission from Ref. [36]; Copyright (2019), American Chemical Society).

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dered channels, tunable energy levels, extensive π-electron delocalization and micro-fiber morphology under scanning electron microscopy, they could be used as photocatalysts for photocatalytic hydrogen production. At 0.2 V versus RHE, the photocurrent of g-$C_{18}N_3$-COF reached up to about 45 μA·cm^{-2}. Under the irradiation of the Xenon lamp at 420 nm, the photocatalytic hydrogen evolution rate was 14.6 μmol·h^{-1}, which was superior to similar materials.

In the same year, Thomas *et al*. modified the synthesis conditions and obtained vinylene-linked COF with the similar structures as well.[37] They also firstly reported that the columnar π-π two-dimensional stacking structure of COFs under the ultraviolet/visible light irradiation for a long time would undergo the [2+2] cycloaddition reaction of carbon-carbon double bonds between adjacent layers. Although the crystallinity of these COFs might disappear after irradiation, it still maintained a relatively high specific surface area. Later they improved the synthesis method of the reported COF-701. Under the catalysis of trifluoromethanesulfonic acid, a mixed solvent of methanol and acetonitrile was used to develop the two-step one-pot method, which firstly combined acetonitriles in trimerization and then made the condensation with aromatic aldehydes.[8] This method was not only applicable to other aldehyde monomers, but also avoided the side reactions caused by base catalysis, opening up a novel, inexpensive, and scalable route to obtain vinylene-linked COFs from acetonitrile directly. For the above [2+2] cycloaddition phenomenon, Perepichka *et al*. conducted further research.[38] They found that the three-dimensional porous crystal polymers formed after irradiation could partially reconvert to the original two-dimensional COFs networks at 200 °C, and still maintained good crystallinity, indicating the reversibility of this photo-crosslinking (Fig. 12). Simultaneously, this two-dimensional to three-dimensional transformation was sensitive to the environment and would be inhibited in the presence of water and proton solvents. The resulting differences were mainly manifested in the changes of mechanical and electronic properties, including peeling, blue shift of ultraviolet absorption spectra, photoluminescence, band structures and different acid doping behaviors. Later, they further expanded the types of COFs constructed from these monomers, which exhibited strong fluorescence.[39] Their quantum yields and emission colors depended on the surrounding environments, and the significant red shift and attenuation were observed in polar solvents. Therefore, they had great potentials for applications in the fields of semiconductors and sensors.

In 2020, Zhang *et al*. prepared two COFs by using 2,4,6-trimethyl-1,3,5-triazine and two aldehyde monomers containing triazine core through Knoevenagel condensation.[40] This structure increased the density of the triazine units, resulting in a highly crystalline honeycomb-like framework formed by the layered stacking of hexagonal lattice polymers. Under scanning electron microscope (SEM), it exhibited a clear nanofiber morphology with a diameter of approximately 80 nm and a length of several micrometers. These COFs fibers could be easily assembled with SWCNTs to form COFs/carbon nanotube (CNT) films with excellent mechanical processing properties. The supercapacitors prepared using this film have many characteristics, such as high surface capacitance, large working voltage output, high volumetric energy density and excellent recycling ability.

In 2022, Wei *et al*. conducted a detailed study to explore the structure-effect relationship of different building blocks by modifying the central core of the aldehyde monomers, such as triphenylamine, benzene and triazine.[41] Although the distorted configuration of triphenylamine would sacrifice the planarity of the entire COFs, it was beneficial for the intramolecular charge transfer process and reduced the possibility of aggregation-induced quenching. Based on the above research, Han *et al*. prepared two sp^{2}C-COFs by conducting the reaction of 2,4,6-trimethyl-1,3,5-triazine with two different aldehydes containing triphenylamine under the catalysis of NaOH.[42] Under the irradiation of visible light, the lone electron pairs on the nitrogen atoms in both structures could be delocalized through photo-induced electron transfer throughout the whole structure. It formed stable free radical cations and photogenerated electrons, which could be used for oxidative organic transformations later.

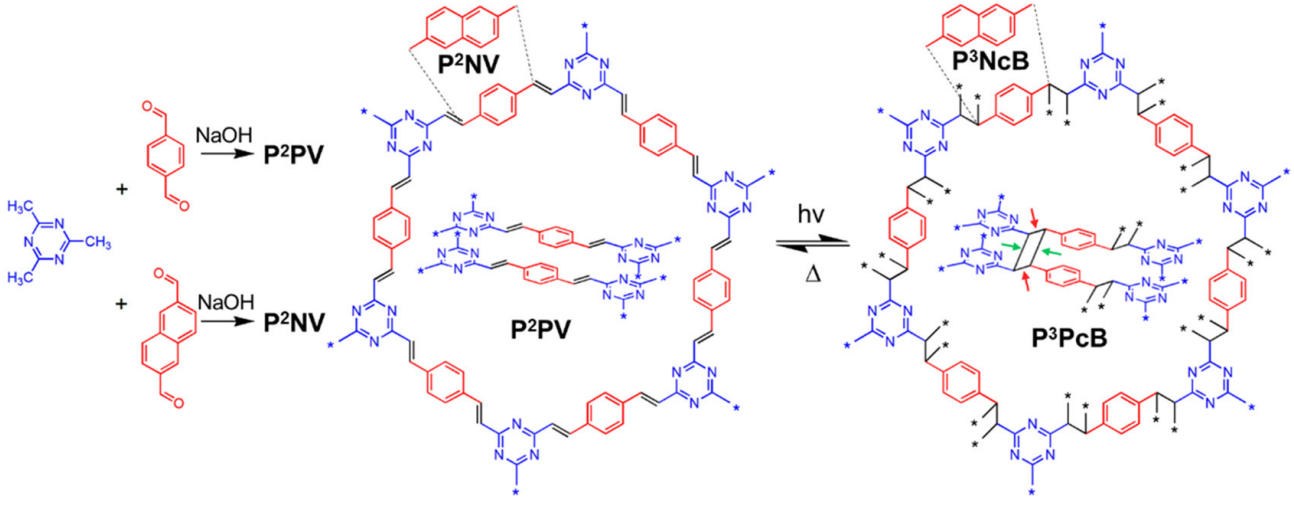

Fig. 12 The photoinduced [2+2] cycloaddition and thermal cycloreversion (Reproduced with permission from Ref. [38]; Copyright (2019), American Chemical Society).

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In 2025, Yu *et al*. collaborated with Zhang *et al*. to conduct detailed research on the influence of different catalysts on the stacking mode of COFs.[43] When using EtONa as the catalyst, *g*-$C_{33}N_3$-COF was in AA stacking. However, when using the LiOH as the catalyst, it was in AB stacking. Such differences may be due to the presence of lithium ions promoting the Lewis acid-base interaction between Li and the nitrogen atoms on the triazine unit, thereby causing the triazine unit to be in a charged state, increasing the total stacking energy of the crystal. Moreover, the change in stacking mode directly led to the significant differences in the photophysical properties between the two COFs, thus exhibiting different activities in photocatalytic H_2O_2 production.

3.2.5 Ionic monomers

As a class of high-value functional molecules, pyridinium salts are commonly used in various fields, such as ionic liquids, antibacterial agents, electrochromic and energy storage. After the quaternization of pyridine ring, the methyl group adjacent to the nitrogen atom can be activated and can react with aldehydes to form various *π*-conjugated molecules with vinylene linkages through the Knoevenagel condensation, which has been repeatedly confirmed by the previous studies.[44–46] Inspired by this, in 2021, Zhang *et al*. were the first to report the construction of vinylene-linked COFs using trimethyl quaternary pyridine salts as monomers.[47] The key active monomers (ETMP-Br/ETMP-I), which were prepared from 2,4,6-trimethylpyridine in acetonitrile, reacted with two aromatic aldehydes containing triazine groups, in a mixed solution of DMF and 1,2-dichlorobenzene under the catalysis of dimethylamine, to obtain ionic COFs with high crystallinity and specific surface area (Fig. 13). They also found that, due to the existence of dipole interactions between adjacent layers and the coulombic repulsion between the pyridine units, the pyridine nitrogen atoms in the interlayers were arranged longitudinally at a 120° angle, in order to minimize the energy of the entire polycrystalline system. The regular and permanent nanochannels, and positively charged rigid framework of these ionic COFs could uniformly composite with polyethylene oxide and lithium salts, such as lithium bis((trifluoromethyl)sulfonyl)azanide. The prepared solid-state electrolyte has an ionic conductivity of 2.72×10^{-3} S·cm^{-1} at a high temperature of 100 °C.

Subsequently, they focused on the commercially available

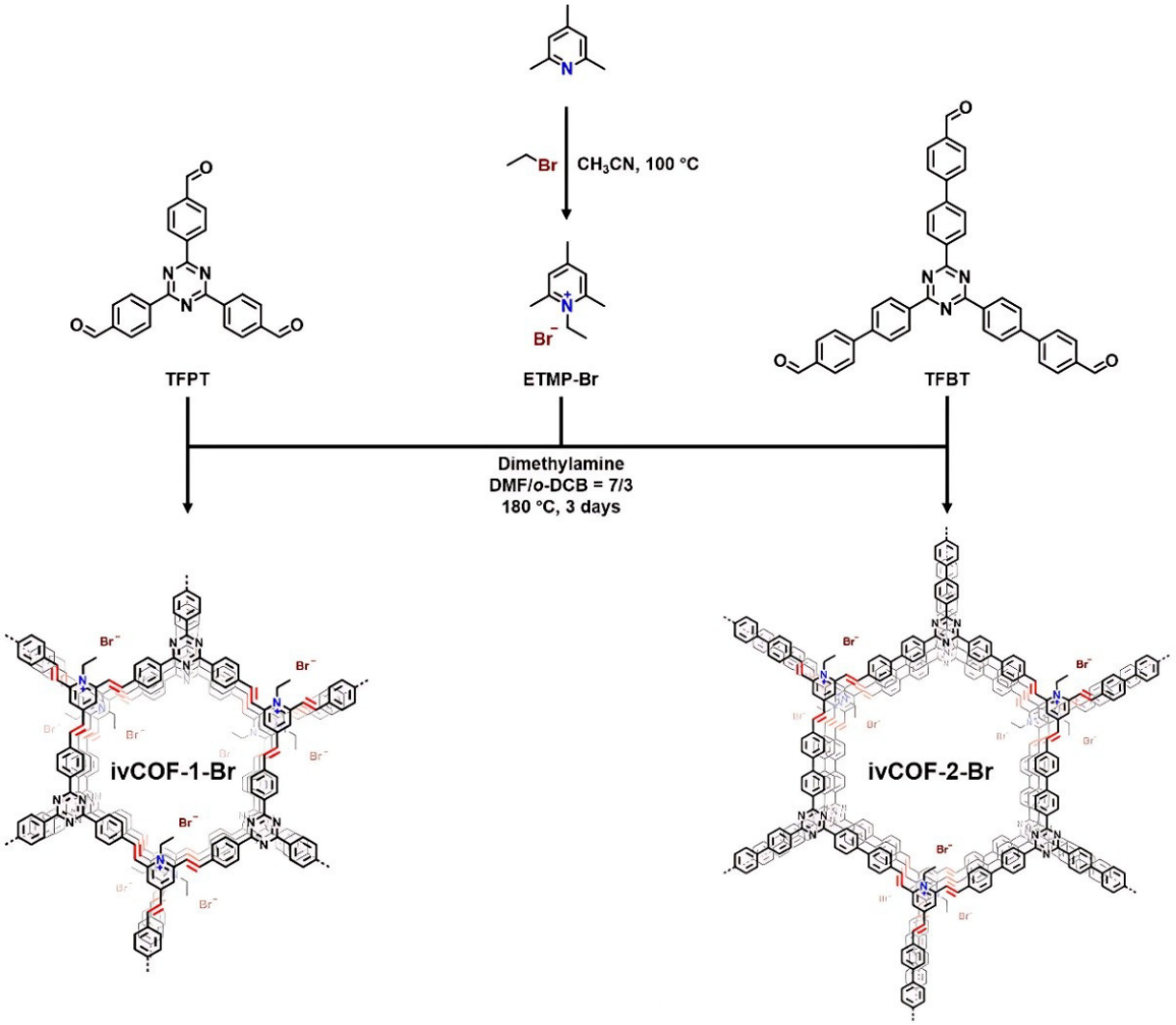

Fig. 13 Synthesis and structures of ivCOF-1-Br and ivCOF-2-Br (Reproduced with permission from Ref. [47]; Copyright (2022), Wiley-VCH).

monomer 2,4,6-trimethylpyrylium tetrafluoroborate and investigated its methyl activation strategies, isoelectronic structural transformation and semiconductor properties at both molecular and polymeric levels.[48] At the molecular scale, the condensation with benzaldehyde, catalyzed by acetic acid, yielded triphenylethylene-substituted pyrylium, which was subsequently converted to a neutral pyridine derivative *via* nucleophilic attack by ammonia. Building upon the synthesis conditions of the model compounds, systematic screening of solvents, temperatures and catalysts led to the identification of *p*-toluenesulfonic acid as the optimal catalyst for the condensation between the core monomer and aromatic aldehydes, resulting in cationic vinylene-linked COFs. Subsequent *in situ* substitution of the oxonium ions with nitrogen atoms, using ammonia as a nucleophile reagent, converted these ionic COFs into neutral pyridine-based COFs. Based on their differing semiconductor behaviors, their band structures were investigated and distinct photocatalytic applications were designed according to their respective attributes. Under visible-light irradiation, the pyrylium COFs and pyridine COFs functioned as an oxidant and a reductant, respectively, generating corresponding intermediates or reactive species, that effectively catalyzed subsequent cyclization reactions to form trisubstituted pyridine derivatives.

In 2023, Xu and colleagues further expanded the types of ionic vinylene-linked COFs.[49] They used *N*-sulfopropyl-2,4,6-trimethylpyridine as the core monomer and 4-dimethylaminopyridine (DMAP) as the efficient catalyst. By using the green hydrothermal synthesis method, they directly prepared high crystalline zwitterionic vinylene-linked COFs through Knoevenagel condensation with aromatic aldehydes containing triazine units (Fig. 14). This condition was also applicable to the preparation of other quaternary pyridine salt COFs. Through detailed theoretical calculations and experi-

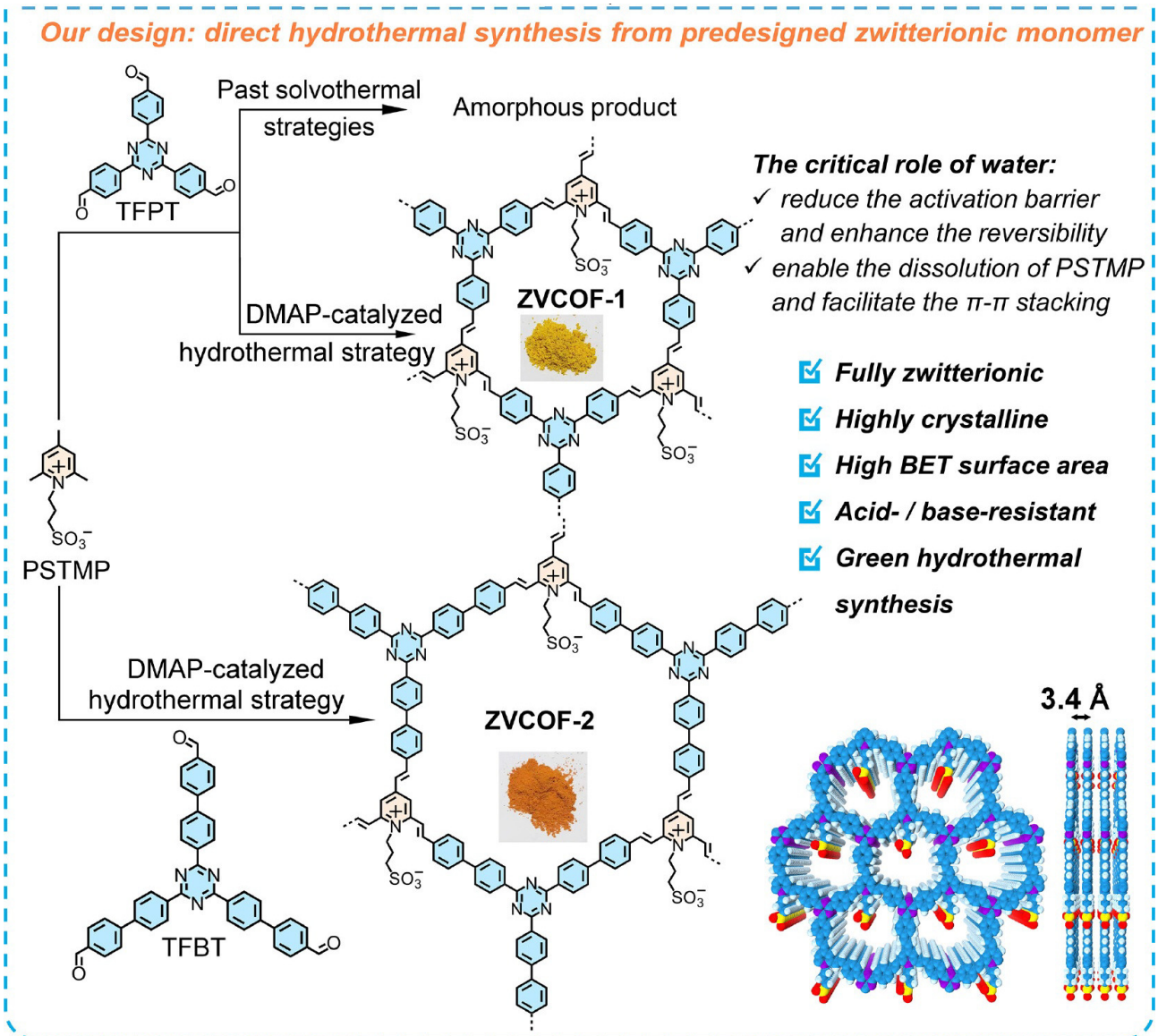

Fig. 14 Schematic diagram for synthesizing ZVCOF-1 and ZVCOF-2 and their structures (Reproduced with permission from Ref. [49]; Copyright (2023), American Chemical Society).

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ments, they demonstrated that the efficient catalytic activity of DMAP and the unique role of water together promoted the formation of the high crystalline zwitterionic COFs. The addition of water decreased the activation energy, improved the reversibility of the reaction, and promoted the ordered polymerization on the plane. It also hydrated the zwitterionic sites, facilitated layered stacking, and thereby obtained the resulting COFs with high crystallinity and specific surface area. The prepared COFs could be simply ultrasonically exfoliated to obtain ultrathin crystalline zwitterionic two-dimensional polymer nanosheets being dispersed stably in water. Benefiting from its good π-conjugated structure and hydrophilic property, the prepared nanosheets exhibited a photocatalytic hydrogen production rate of 2052 μmol·h^{-1} under visible light irradiation and the apparent quantum yield at 420 nm could reach up to 47.1%, which was superior to the previously reported COFs. Moreover, this ionic COFs could be deposited on nylon carriers as a photocatalytic film device and its photocatalytic hydrogen production performance could reach up to 402.1 mmol·h^{-1}·m^{-2}. Based on these results, the resultant COF termed ZVCOF-1 features suitable band structures, highly ordered and conjugated backbones, and abundant hydrophilic side chains, which efficiently promote the photocharge generation, separation and transfer upon the light irradiation, which was necessary of high-performance photocatalysts for water splitting.

3.2.6 Methylpyridine derivatives

Pyridine, as a nitrogen-containing six-membered heterocyclic aromatic compound, acts as a Lewis base and has wide applications in many fields, such as catalysis, coordination and organic semiconductors. It has been previously confirmed that the α-C—H in 2,4,6-trimethylpyridine could be activated through quaternization to undergo the Knoevenagel condensation reaction. Meanwhile, *N*-acylpyridinium compounds are highly reactive intermediates formed during pyridine-catalyzed anhydride hydrolysis, which also serve as efficient acylating agents prepared from pyridine and acyl donors. Therefore, the acylation of methylpyridine derivatives involves the possible reversibility of activating the α-C—H.[50] In 2021, Zhang *et al*. used 2,5-dimethylpyrazine as the core monomer and synthesized nitrogen-rich vinylene-linked COFs under catalysis of benzoic anhydride at 200 °C.[51] To better elucidate the underlying mechanism of this method, in 2022, Zhang *et al*. firstly proposed the mechanism of acylating agent activation of pyridyl methyl groups, which is that as a Lewis base methylpyridine catalyzes the hydrolysis of benzoic anhydride by forming the *N*-benzoylpyridinium ion intermediates.[41,52] Simultaneously, benzoylation significantly enhances the electron-deficient nature of the pyridine ring, and thereby increases the acidity of the α-H on the pyridyl methyl group. Consequently, the resulting conjugated benzoyl base can capture the proton from the methyl group. Subsequently, the protonated aldehyde undergoes electrophilic addition in an acidic environment, generating the enamine intermediate, which then eliminates water molecule to form the vinylene bond. The formyl group hanging on the pyridine ring can be removed by neutralization with a base to yield the neutral framework. Based on the above acylation mechanism, they used 2,2',6,6'-tetramethyl-4,4'-bipyridine as the core monomer and polymerized it with aldehydes of different C_2 symmetries under the catalysis of benzoic acid and benzoic anhydride to obtain two rhombic pore structures with high crystallinity and specific surface area, which also exhibited high catalytic activity in photocatalytic hydrogen production (Fig. 15). In the same year, they selected the more common 2,4,6-trimethylpyridine as the core monomer and used the same method with aromatic aldehydes of different symmetries to expand the variety of vinylene-linked COFs.[53] They also discussed in depth the effects of different acylating agents and reaction temperatures on crystallinity, further refining the acylation mechanism and expanding the application of COFs in the field of thermal catalytic esterification.

In 2023, they designed and synthesized the D_{3h}-symmetric hexamethyl-functionalized monomer comprising three 2,6-dimethylpyridine moieties linked at the *meta*-positions of a benzene ring.[54] Then, this monomer was condensed with linear aldehyde monomers of varying lengths. The resulting two COFs exhibited high crystallinity and large specific surface areas, consisting of alternating hexagonal microporous and mesoporous channels. This heteropore topological design enabled each large hexagonal channel to be circumferentially enclosed by alkene-linked donor-acceptor (D-A) segments, forming an extended π-conjugated system that traversed the pyridine units at the 2,6-positions and the phenyl/biphenyl groups at the *para*-positions. As a result, π-delocalization is confined around the nanochannels, endowing the synthesized COFs with a unique capability of generating reactive oxygen species (ROS) upon green light excitation. This property facilitated highly chemo-selective and shape-selective photocatalytic bromination of aromatic compounds with excellent recyclability and reusability.

In 2023, Liang and Zhang *et al*. collaboratively synthesized two vinylene-linked COFs with ultra-microporous dimensions (<1 nm) *via* condensation of the tetramethylpyrazine and linear aromatic dialdehydes under catalysis by benzoic anhydride.[55] Both COFs could be well dispersed in water, forming negatively charged stable submicron particles. This unusual behavior could be attributed to the weak interactions and charge transfers between the framework and the water molecules confined within the micropores, alongside protonation/deprotonation effects that enable tunable aggregation behavior. Consequently, these COFs exhibited highly selective and pore-size-dependent colorimetric responses toward various anions with different pKa values. Later that year, Abbaspourrad *et al*. focused on nitrogen-rich aromatic systems and employed 3,6-dimethyltetrazine as the core monomer.[56] Under the catalysis of trifluoroacetic acid in a mixed solvent system of mesitylene/1,4-dioxane/acetonitrile, they condensed it with various aromatic aldehydes to obtain two highly crystalline, stable and narrow-bandgap vinylene-linked COFs. As photocatalysts, these COFs maintained high conversion rates in reactions, such as hydroxylation of arylboronic acids and oxidative coupling of benzylamines, while demonstrating excellent cycling stability. In terms of specific detection, these COFs exhibited selective responsiveness to various acid vapors, undergoing reversible visible color changes exclusively upon the exposure to HCl vapor, along with other distinct and rapid responses in different acid-base environments. Regarding environmental safety, the protonat-

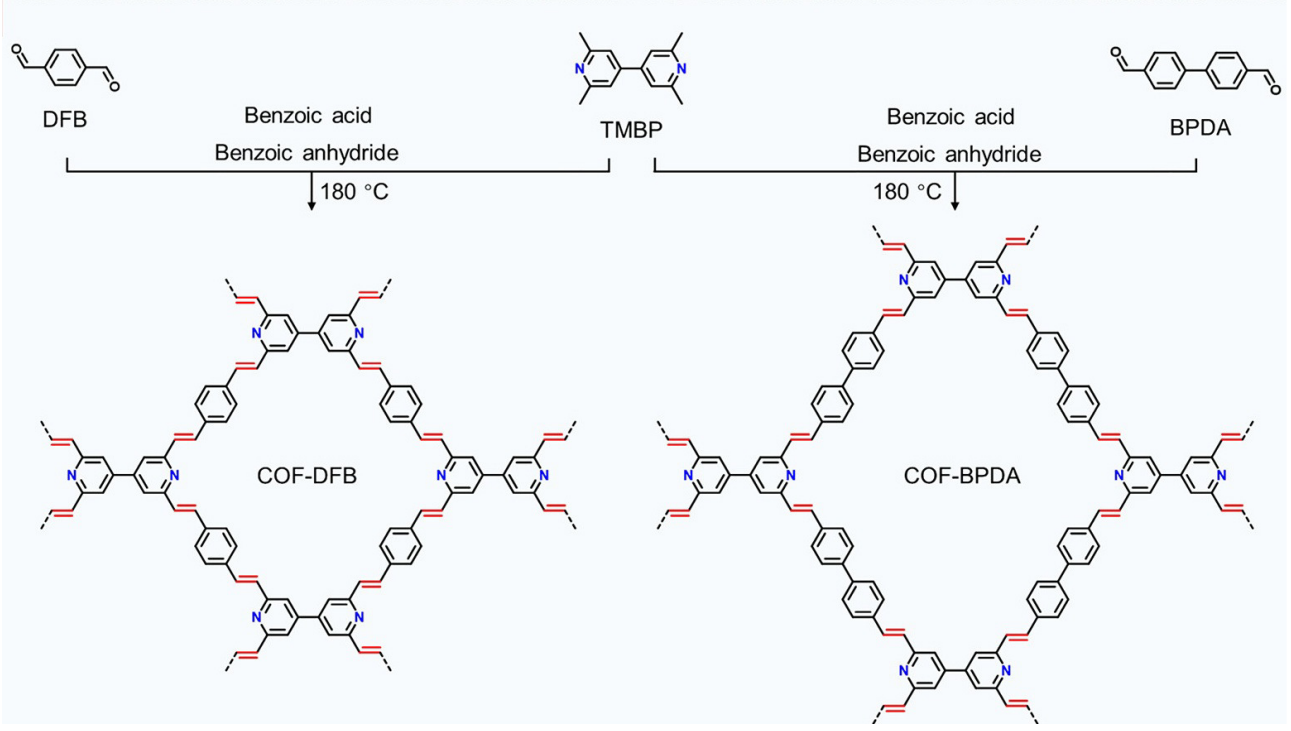

Fig. 15 Synthesis and structures of COF-DFB and COF-BPDA (Reproduced with permission from Ref. [52]; Copyright (2022), American Chemical Society).

ed form of these COFs could function as both catalyst and Brønsted acid, enabling rapid degradation of 5-nitro-1,2,4-triazol-3-one in industrial wastewater under light irradiation.

In 2024, Zhang *et al*. utilized 3,6-dimethylpyridazine as a linear monomer under catalysis by benzoic acid/benzoic anhydride to construct vinylene-linked COFs.[57] The two adjacent sp^2-hybridized nitrogen atoms functionally acted as a "*cis*-azo" configuration, effectively promoting Knoevenagel condensation with triformyl-substituted aromatic derivatives. The resulting ordered channels contained two fully exposed lone electron pairs provided by the pyridazine units, which served as strong hydrogen-bond accepting sites. Moreover, the pore size was suitable to facilitate water molecule transport, endowing the synthesized COFs with exceptional water uptake performance. Even at relatively very low humidity, they exhibited the water absorption capacity of 0.26 g/g, surpassing the best performance reported thus so far for any COFs. Furthermore, hydration/dehydration cycling tests demonstrated outstanding hydrolytic stability, durability and adsorption-desorption retention in both COFs. The other two groups also developed a 1,2-diazine-containing molecule 2,5-dimethyl-1,3,4-thiadiazole as a ditopic electron-deficient monomer, which was condensed with 1,3,5-tris(4-formylphenyl)triazine for preparation of vinylene-linked thiadiazole-based COFs using trifluoromethanesulfonic acid or benzoic anhydride/benzoic acid as catalysts. Related to their vinylene-linked fully conjugated frameworks, the resultant COFs exhibited high chemical stability and superior photoelectrochemical properties. Under visible-light irradiation, such thiadiazole-based COF showed an impressive photocurrent of up to about 14.5 $\mu A \cdot cm^{-2}$ at 0.3 V versus RHE, and a high photocatalytic hydrogen evolution activity with 7314 $\mu mol \cdot h^{-1} \cdot g^{-1}$ under visible light irradiation.[58,59]

Subsequently, in collaboration with Xu *et al*., they incorporated pyridine units with different connectivity patterns, such as pyridine, 3,3′-bipyridine and 4,4′-bipyridine, into vinylene-linked COFs.[60] This structural modulation influenced the oxygen binding sites in the non-polar regions and successfully tuned their selectivity toward the oxygen reduction reaction (ORR). This behavior was attributed to their differing oxygen binding affinities, which altered the interaction strength between intermediate OH* species and catalytic sites, a conclusion further supported by theoretical calculations. Later, Li *et al*. employed a series of tetrahedral building units with various functional backbones, such as phenyl, benzothiadiazole and benzoxadiazole, to construct vinylene-linked COFs.[61] By varying the donor and acceptor units, they were able to modulate the overall optoelectronic properties precisely.

3.2.7 Carbonyl-containing monomer

In 2022, Huang *et al*. employed *s*-indacene-1,3,5,7(2*H*,6*H*)-tetrone as the core monomer and condensed it with various fused-ring aromatic aldehydes under catalytic conditions using piperidine or acetic acid in mixed solvents comprising DMAc and either 1,2-dichlorobenzene or *n*-butanol, yielding two vinylene-linked COFs (Fig. 16).[62] Owing to their well-ordered two-dimensional crystalline structures, high porosity, elevated electrical conductivity and abundant carbonyl units serving as redox-active sites, the as-synthesized COFs were demonstrated to function as high-performance cathode materials in lithium-ion batteries. During electrochemical testing, TFPPy-ICTO-COF delivered a high specific capacity of 338 $mAh \cdot g^{-1}$ at 0.1 C, along with remarkable capacity retention of 100% after 1000 cycles, highlighting the exceptional stability of the synthesized material.

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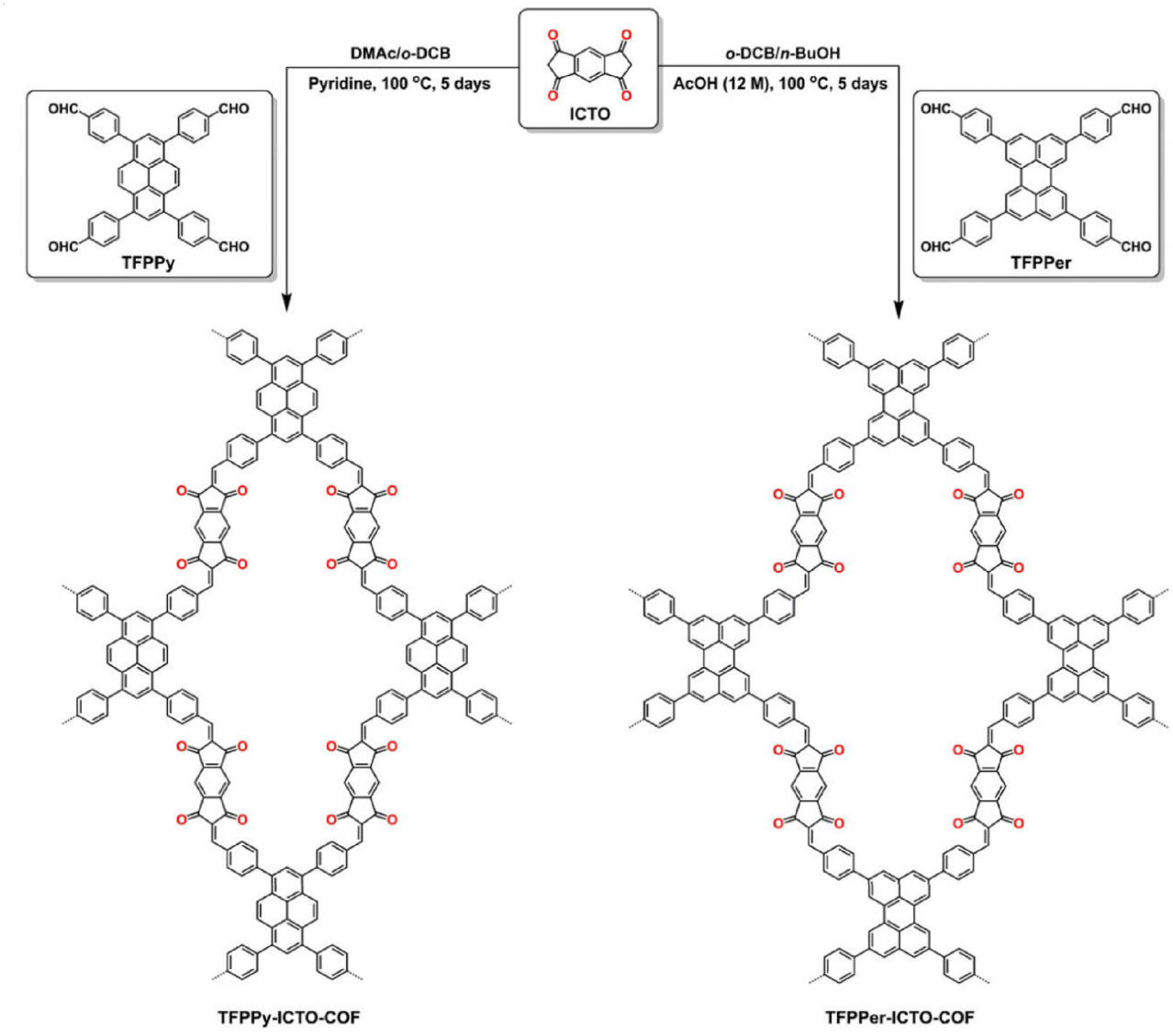

Fig. 16 Schematic diagram for construction of TFPPy-ICTO-COF and TFPPer-ICTO-COF (Reproduced with permission from Ref.[62]; Copyright (2023), American Chemical Society.)

In 2024, Zhang *et al*. using 2,5-dibutyl-3,6-dimethyl-1*H*,2*H*,4*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DM-DPP) as the key monomer successfully developed two novel two-dimensional vinylene-linked COFs.[63] DPP as a functional small molecule has previously been incorporated into COFs *via* post-synthetic modification. In contrast to such conventional approaches, the electron-deficiency nature of DPP was directly exploited here to activate the adjacent methyl groups. Through extensive condition screening in aqueous medium using L-proline and 4-dimethylaminopyridine as catalysts, an optimized synthetic route was established for the target COFs *via* DM-DPP-promoted dynamic polycondensation. Model reactions were employed to investigate the dynamic covalent chemistry involved in the vinylene linkages formation, confirming the existence of a self-healing process and enabling the proposal of a plausible condensation mechanism. The two highly crystalline COFs feature a two-dimensional framework constructed *via* direct linkage between the DPP core and vinylene bonds, facilitating extensive π-delocalization both in-plane and vertically. As a result, they exhibit narrow bandgaps of approximately 1.0 eV and outstanding light-harvesting capabilities extending from the visible to near-infrared regions (NIR-I and even NIR-II). Under illumination with different light sources, these COFs demonstrate highly sensitive and cyclically stable photothermal responses.

3.3 Post-synthetic Modification and Functionalization

Compared to other dynamically linked COFs, vinylene-linked COFs inherently exhibit superior chemical and structural stability. Therefore, post-synthetic modification and functionalization efforts primarily focus on enhancing specific properties through various strategies, such as coordination, cyclization, reduction, oxidation and introduction of additional functional groups. In 2020, Qiu *et al*. condensed 2,2',2"-(benzene-1,3,5-triyl)tris(acetonitrile) with aromatic aldehydes to synthesize vinylene-linked COFs containing cyano groups.[64] These cyano moieties were subsequently converted into amidoxime groups using excess

$NH_2OH{\cdot}HCl$, enabling highly efficient extraction of UO_2^{2+}. Moreover, the modified COFs allowed for real-time sensitive detection of radioactive elements, efficient extraction and full regeneration of the materials simply by adding carbonates, thereby thus expanding the potential of COFs in environmental remediation. In the same year, Gu *et al*. condensed benzyl cyanide-based active monomers with hydroxy-substituted aldehydes.[65] Under oxygen and strong base, the material underwent sequential cyanide migration, ring closure and oxidation to form heteroaromatic cyano-substituted benzofuran-linked COFs. Subsequent post-synthetic modification fully converted the cyano groups into carboxylic acids while preserving the original framework and porosity. The acidified COFs exhibited a proton conductivity of 4.35×10^{-2} $S{\cdot}cm^{-1}$, demonstrating their practical utility.

In 2024, Luo *et al*. condensed 2,2′-bipyridine-5,5′-dicarbaldehyde with 2,2′,6,6′-tetramethyl-4,4′-bipyridine under catalysis by benzoic acid and benzoic anhydride, obtaining a fully pyridyl-based vinylene-linked COF.[66] After ruthenium coordination, the resulting material exhibited strong cross π-conjugation, which not only activated coordinated oxygen, stabilized oxygen vacancies and promoted reaction kinetics, but also maintained overall framework stability. In acidic electrolyte, it showed a high oxygen evolution activity of 2659.3 $A{\cdot}g^{-1}$, which is 32 times higher than commercial RuO_2 along with long-term durability exceeding 280 h. Subsequently, Yaghi *et al*. incorporated an azide-functionalized aldehyde monomer into the cyano-substituted vinylene-linked COF-999 and modified the framework with a ring-opening polymerization initiator (Fig. 17).[67] Polyamines were then introduced into the pores *via in situ* polymerization. The modified COF demonstrated CO_2 capture capacities of 0.96 $mmol{\cdot}g^{-1}$ under dry conditions and 2.05 $mmol{\cdot}g^{-1}$ at 50% relative humidity. And even after more than 100 adsorption–desorption cycles in ambient air, the material retained its performance without any degradation.

4 APPLICATION OF VINYLENE-LINKED COFS IN THE FIELD OF SEMICONDUCTORS

Vinylene-linked COFs possess a range of intriguing features including precise framework ordering at molecular level, extended π-conjugated skeletons, exceptional chemical stability and tunable molecular design, which collectively enable their diverse functionalities and broad applications. The delocalization of π-electrons across the vinylene-linked frameworks confers distinctive semiconductor properties on these COFs, rendering them superior to other dynamically covalently linked COFs in performances related to photocatalysis, electrocatalysis and electrochemical applications.

4.1 Photocatalysis

COFs have emerged as prominent materials in the field of photocatalysis due to their well-ordered stacking structures, permanent porosity, recyclability, abundant semiconductor activity and excellent chemical stability. Compared to other linking motifs in COFs, C=C linked sp^2-C COFs exhibit high conjugation structure, which facilitates π-electron delocalization and efficient transport, thereby promoting the charge carrier mobility.[68] In 2020, Cooper *et al*. introduced bipyridine groups into the framework and performed post-synthetic modification with rhenium coordination compound to enhance the photocatalytic CO_2 reduction performance (Fig. 18).[69] The coordinated COFs achieved a CO production rate of 1040 $\mu mol{\cdot}h^{-1}{\cdot}g^{-1}$ after 17.5 h of illumination. Following dye sensitization, this performance was further improved to 1400 $\mu mol{\cdot}h^{-1}{\cdot}g^{-1}$ within 5 h, with high selectivity of 86% for CO over H_2. Lang *et al*. employed trimethyltriazine as a core unit and modulated the optoelectronic properties by varying the conjugation length of aldehyde monomers.[70] The insertion of vinylene linkages alleviated steric hindrance and provided more delocalized π-electrons, endowing the resulting COFs with superior performance in the photocatalytic oxidation of organic sulfides to sulfoxides using molecular oxygen. Subsequently, Dong *et al*. synthesized two vinylene-linked COFs using 2,9-dimethyl-1,10-phenanthroline as

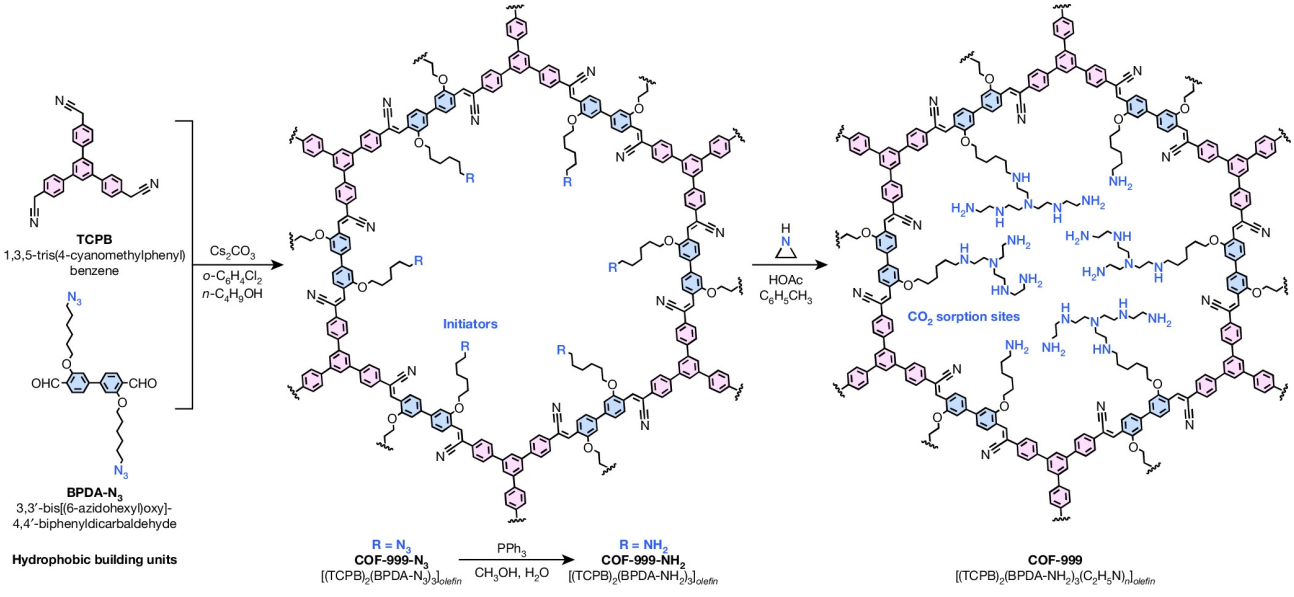

Fig. 17 Synthesis and post-modification methods of COF-999 (Reproduced with permission from Ref. [67]; Copyright (2025), Springer Nature).

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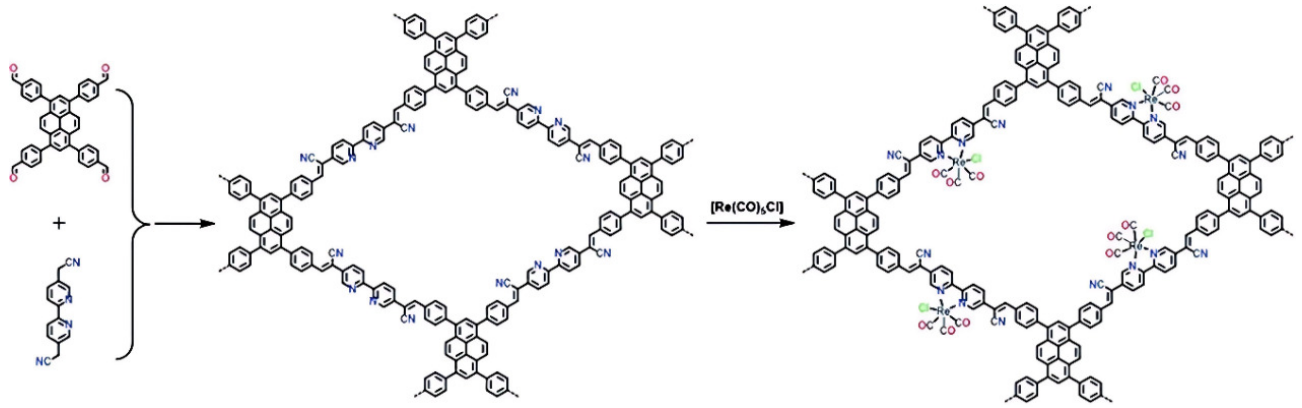


Fig. 18 Synthesis of Bpy-sp2c-COF and Re-Bpy-sp2c-COF (Reproduced with permission from Ref. [69]; Copyright (2020), Royal Society of Chemistry).

a core monomer and aromatic aldehydes in the presence of trifluoromethanesulfonic acid as the catalyst.[71] Between them, PVCOF-1 exhibited broad visible-light absorption with an absorption edge beyond 600 nm and achieved outstanding hydrogen and oxygen evolution rates of 11525 and 2056 $\mu mol \cdot g^{-1} \cdot h^{-1}$, respectively, significantly surpassing those of the photocatalysts based on previously reported bifunctional COFs.

Zhang *et al*. incorporated both trimethyltriazine and multiple aldehyde monomers into COFs simultaneously, engineering a dual-reactive-center system wherein anthracene served as the reduction site and benzothiadiazole as the oxidation site, distributing within a triphenylethylene-functionalized triazine framework.[72] The exceptional electron donating and accepting capabilities of the dual centers ensured efficient charge separation, resulting in long-lived photogenerated electron-hole pairs and enabling highly universal, efficient and stable organic transformations of photocatalytic difluoromethylation. Subsequently, Mi *et al*. introduced alkyne units into aldehyde monomers to synthesize two vinylene-linked COFs.[73] The regularly aligned triazine and acetylene units forming donor-acceptor structures effectively promoted charge separation and suppressed charge recombination, leading to superior performance in photocatalytic hydrogen peroxide production compared to most analogous materials. Later, Mi *et al*. modulated the band gaps of COFs by preparing aromatic alkynyl aldehydes with different substituents, extended the conjugation length of the methoxy groups incorporated COFs, reduced interfacial resistance and enhanced hydrophilicity of the COFs, thereby endowing them with high catalytic efficiency in photocatalytic organic transformations, such as thiocyanation of indole derivatives (Fig. 19).[74]

In 2022, Liu *et al*. developed a gradient heating strategy to synthesize highly crystalline vinylene-linked COFs through the condensation of terephthalonitrile as an active monomer with aromatic aldehydes.[75] The incorporation of cyano-vinylene linkages into the framework not only enhanced π-electron coupling and broadened the visible-light absorption range, but also created independent electron and hole channels for efficient charge carrier transport and separation. The synthesized COFs exhibited excellent surface hydrophilicity, which improved their dispersibility in water and facilitated interactions between the photocatalyst and water/sacrificial electron donors. After platinum doping, the material demonstrated a high hydrogen evolution rate of 107380 $\mu mol \cdot g^{-1} \cdot h^{-1}$. In 2023, the same group successfully fabricated two types of COFs with high crystallinity and large specific surface areas *via* a multi-component synthesis strategy.[76] These structures incorporated electron-rich benzotrithiophene as the donor and electron-deficient triazine as the acceptor, connected to benzene through vinylene and imine linkages, respectively. Comprehensive studies based on photoelectrochemical properties and theoretical calculations revealed that the three-component D-π-A architecture effectively modulated the semiconductor band structure and optoelectronic properties, promoted exciton dissociation, and enhanced charge carrier transfer and separation, thereby significantly improving photocatalytic hydrogen evolution activity. As a result, the vinylene-linked COFs achieved an exceptional hydrogen production rate of (70.8±1.9) $mmol \cdot g^{-1} \cdot h^{-1}$ under visible light irradiation, along with outstanding reusability surpassing most COFs-based photocatalysts reported to date.

In 2023, Zhang *et al*. obtained highly crystalline products by reacting dimethylbenzothiadiazole monomers with three different C_3-symmetric aromatic aldehydes under catalysis of benzoic acid and benzoic anhydride.[77] The electron-deficient benzothiadiazole moiety endowed the resulting COFs with a broad-range light absorption, suitable energy levels for photocatalytic H_2 and H_2O_2 production, and high photoactivity. Moreover, all three COFs were capable of selectively generating singlet oxygen under visible light to catalyze the photocatalytic oxidation of methyl phenyl sulfide derivatives, thereby expanding the scope of research in photocatalysis.

Subsequently, Wang *et al*. incorporated thiadiazole groups into the framework *via* different dynamic covalent bonds with aldehydes.[59] Comparative studies revealed that the vinylene-linked COFs exhibited superior photoelectronic properties compared to fully or partially imine-linked COFs, which was attributed to the low exciton binding energy in the vinylene-linked structures, thereby promoting exciton dissociation and charge separation. Shortly afterward, Zhang *et al*. synthesized a representative complex monomer based on dimethyl-diazapyrene (PAH), in which the two methyl groups adjacent to the nitrogen atoms enhanced solubility and served as reactive linking sites.[78] After verifying the feasibili-

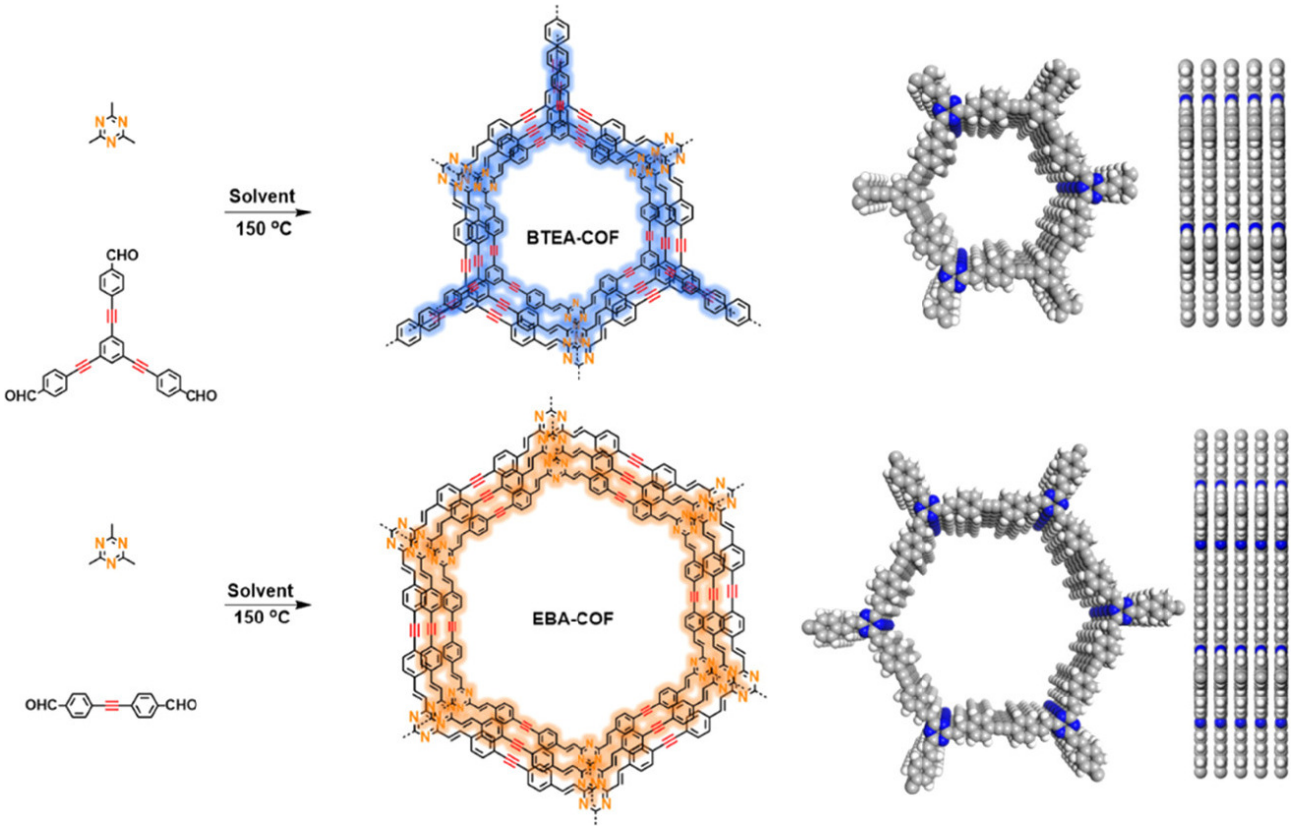
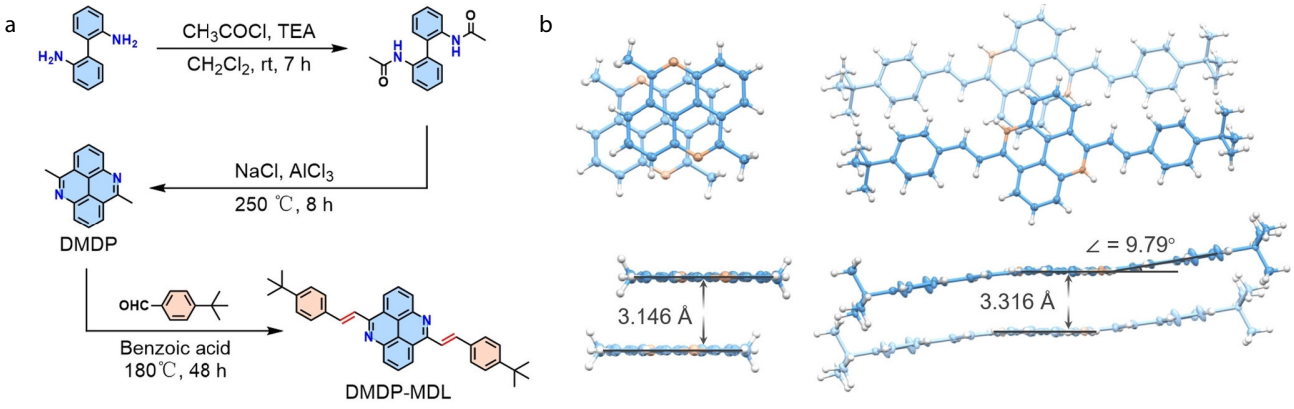


Fig. 19 Schemes of synthetic processes and structures of BTEA-COF and EBA-COF (Reproduced with permission from Ref. [73]; Copyright (2023) American Chemical Society.)

ty of the design through successful synthesis of model compounds, the hetero-fused monomer was condensed with aromatic aldehydes catalyzed by benzoic acid, yielding two-dimensional COFs with high planarity, crystallinity and specific surface area (Fig. 20). Owing to the direct linkage between the PAH building blocks and vinylene bonds, the resulting COFs possessed a spatially extended π-conjugated system and exceptional semiconductor properties. Under light irradiation, they achieved a remarkable H_2O_2 production rate of up to 3820 μmol·g^{-1}·h^{-1} in pure water. When benzyl alcohol was used as a hole scavenger, the yield increased to 17080 μmol·g^{-1}·h^{-1}, surpassing most reported graphene-like materials.

In 2024, Wang *et al*. synthesized two vinylene-linked COFs, namely TMT-COF and TBTN-COF, by condensing benzotrithiophene-based aldehyde monomer with triazine-trimethyl and 3,5-dicyano-2,4,6-trimethylpyridine, respectively.[79] Between them, TBTN-COF exhibited ultrafast intramolecular electron transfer rate and prolonged charge separation lifetime. These remarkable features led to a photocatalytic H_2O_2 production rate of 11013 μmol·g^{-1}·h^{-1}, significantly outperforming the other COF as well as most reported photocatalysts. Furthermore, based on *in situ* infrared spectroscopy (IR) analysis and theoretical calculations, the authors proposed that the incorporation of cyano groups facilitated the formation of the *OOH intermediate, thereby accelerating H_2O_2 generation. In 2025, Wang *et al*. prepared three aldehyde monomers based on terpyridine and tetrapyridyl motifs, which subsequently



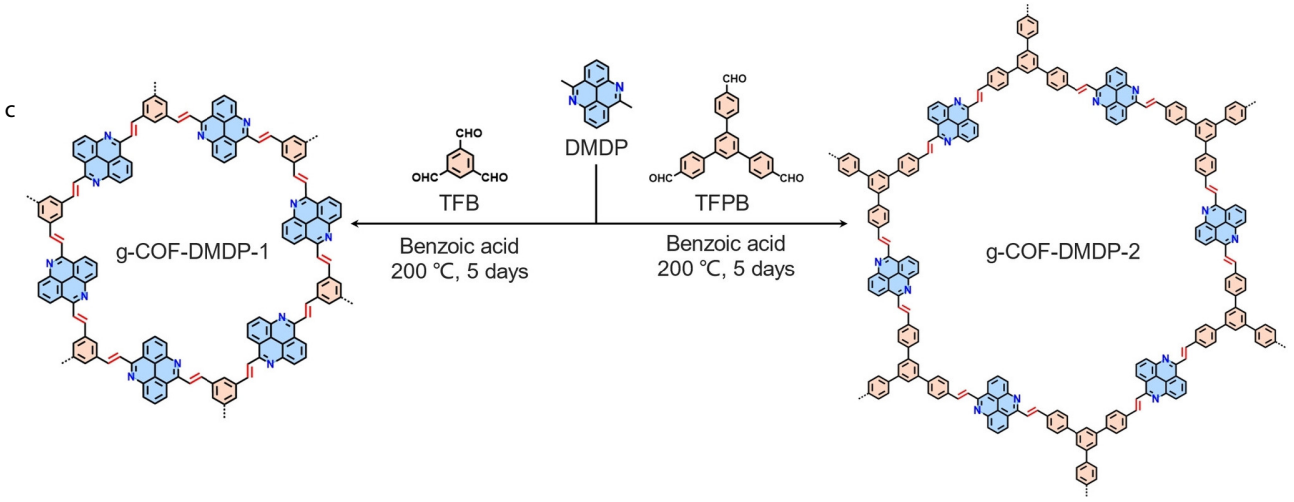


Fig. 20 (a) Synthesis and (b) single crystal structures of key monomer and model compound. (c) Schematic diagram of synthesis of target COFs (Reproduced with permission from Ref. [78]; Copyright (2025), Wiley-VCH).

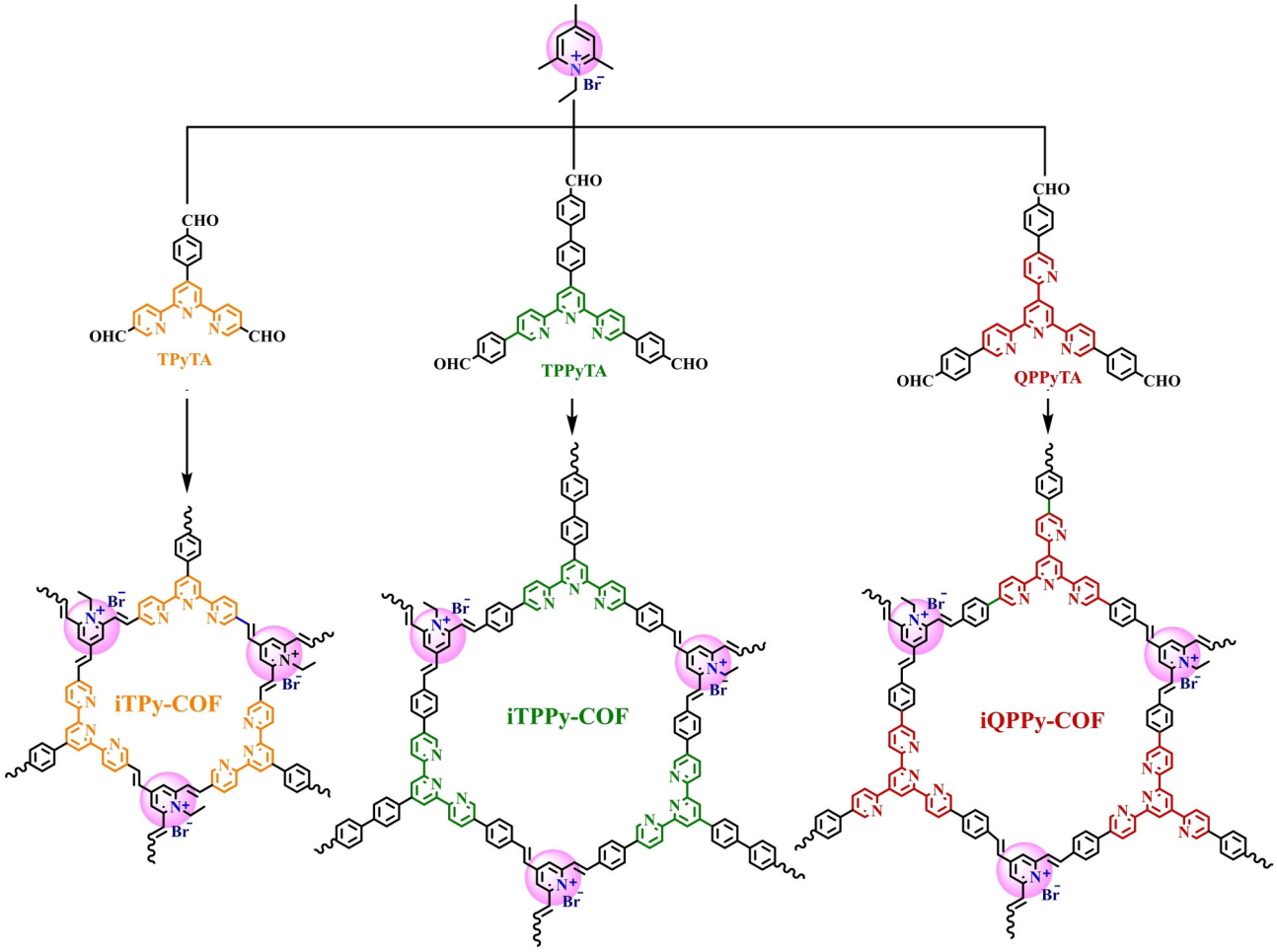


Fig. 21 Synthetic strategy and structures of iTPy-COF, iTPPy-COF and iQPPy-COF (Reproduced with permission from Ref. [80]; Copyright (2025), Wiley-VCH).

reacted with ETMP-Br to obtain nitrogen-rich vinylene-linked COFs.[80] The resulting donor-acceptor cationic COFs demonstrated considerably high visible-light catalytic efficiency. Under conditions of pure water and an oxygen atmosphere, iTPPy-COF achieved a H_2O_2 production rate as high as 7955 μmol·g^{-1}·h^{-1} after one hour reaction. Even in ambient air, the rate remained high at 6249 μmol·g^{-1}·h^{-1}. Additionally, the authors found that varying the arm length and ratio of pyridine

and phenyl rings within the framework significantly influenced photocatalytic performance. Through theoretical simulations and measurements of physical parameters such as fluorescence lifetime, photocurrent intensity and charge transfer impedance, the relationship between electronic structure modifications and structure performance in polypyridine-based cationic COFs was systematically investigated, offering new insights into the design of highly efficient photocatalytic COFs (Fig. 21).

4.2 Electrocatalysis

Vinylene-linked COFs possess long-range ordered layered structures that enable the dispersion of isolated catalytic sites, high porosity that facilitates mass transport, excellent chemical stability, tunable pore sizes and topological skeletons, providing a strong foundation for electrocatalytic applications. However, the inherent poor electrical conductivity of two-dimensional COFs materials often necessitates the introduction of highly mobile charge carriers, metal ion complexes or heteroatom doping, to modulate their electronic structure and then to overcome this limitation. Chen *et al*. employed trimethyltriazine as a building block to synthesize vinylene-linked COFs with high conductivity and stability, which were further complexed with ruthenium ions to enhance its electrocatalytic hydrogen evolution performance.[81] The nitrogen atoms in the triazine unit undergo protonation in acidic media and form stable coordination structures with ruthenium ions, significantly improving the electrical conductivity and stability of the modified material. The resulting system exhibited an overpotential of approximate 200 mV at a current density of 10 $mA{\cdot}cm^{-2}$. In 2024, Xu *et al*. anchored porphyrin units onto the pore walls of a vinylene-linked COF *via* post-synthetic modification.[82] This approach not only preserved the high crystallinity and porosity of the framework but also allowed for the incorporation of abundant metal sites. The vinylene linkages between the framework and catalytic units facilitated efficient charge transfer, while the pore-size confined catalysts within the pores catalyzed the oxygen reduction reaction (ORR), achieving a high half-wave potential of 0.85 V, which was superior to most reported analogues.

4.3 Luminescence

In 2021, Huang *et al*. expanded the structural diversity of COFs by synthesizing a highly emissive vinylene-linked framework through the condensation of 2,7,12-triformyl-5,10,15-triethyltriindole with trimethyltriazine.[83] For comparison, another COF was prepared using 1,3,5-tris(4-formylphenyl)benzene as a building block. This approach enabled a direct investigation into the relationship between molecular structures and properties, such as light absorption/emission, charge transfer and exciton dynamics. The results demonstrated that white light could be achieved simply by coating the COFs onto light-emitting diode (LED) strips or physically blending the two COFs. Time-resolved absorption and emission spectroscopy, combined with theoretical calculations, revealed that the planarity, conjugation, and interlayer stacking of the COFs not only determined their light-harvesting capability but also significantly influenced exciton relaxation pathways and photoluminescence quantum yields.

5 SUMMARY AND OUTLOOK

Covalent organic frameworks (COFs), as an emerging class of porous organic materials connected *via* dynamic covalent bonds, have demonstrated significant application potential across various cutting-edge fields after two decades of development. Compared to traditional linkages, such as boronate esters or imine bonds, vinylene-linked frameworks not only enhance the chemical stability of COFs and improve π-electron delocalization, but also boost multiple physical properties, including semiconductor activity. The key to prepare such COFs lies in the design and synthesis of highly reactive α-methyl monomers. Conventional strategies to obtain sufficiently reactive functional monomers often involve introducing electron-withdrawing groups (*e.g.*, cyano) into the aromatic ring to increase the acidity of adjacent α-hydrogens, a process that typically requires toxic reagents such as cyanides. Therefore, future development of vinylene-linked COFs should focus on exploring novel synthetic strategies, designing new α-methyl-functionalized monomers, optimizing the dynamic covalent chemistry during polymerization and investigating the structure-property relationships of the resulting materials.

For the future development of vinylene-linked covalent organic frameworks, the following aspects deserve attention:

(1) Further enhancement of the dynamic reversibility of the Knoevenagel/aldol condensation reaction through optimization of reaction conditions, such as temperature, catalyst and solvent, thereby improving the self-healing capability during COFs formation to obtain highly crystalline products. Concurrently, it is essential to explore the feasibility of synthesizing vinylene-linked COFs under milder conditions, including lower temperatures or even room temperature, and to develop rapid preparation methods, through microwave irradiation and mechanochemical synthesis approaches.

(2) Investigation into the preparation of COF samples with large crystalline domain, along with the exploration of three-dimensional vinylene-linked COFs by monomer design, structural development and condition screening.

(3) Fabrication of few-layer or even single layer COFs samples *via* interfacial polymerization or top-down exfoliation approaches, and development of thin film COFs to enhance material processability.

(4) Optimization of COFs synthesis conditions to control growth and nucleation processes, enabling the preparation of single polymer crystals.

(5) Exploring the crystallization process of vinylene-linked COFs through the technology on the basis of in situ tools.

(6) Expansion of structural diversity and material functionality through post-synthetic modification of vinylene linkages, thereby broadening the scope of related applications.

BIOGRAPHIES

Bai Xue graduated from Nanjing University in 2001 with B.S. degree and M.S. degree in 2004, majored in Biological Sciences. She pursued her PhD in System Bioinformatics at SUNY-UB, US. Later after she worked as Research Associate at Institute for Clinical PharmacoDynamics in US for two years, she came back China and joined Fudan University as Postdoctoral Fellow. In 2017 after she completed her postdoctoral terms, she started her career as Research Assistant in Shanghai Jiao Tong University and till now.

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Fan Zhang received his BEng degree in electrochemistry from Shanghai Jiao Tong University in 1991, and his PhD in organic chemistry from Jilin University in 2000. After more than eight years of research experience in Germany and the United States, he was promoted to a full Professor in School of Chemistry and Chemical Engineering of Shanghai Jiao Tong University, China. His research interests span from organometallic catalysis and polymerization methodology to organic π-conjugated functional materials and nanocarbons for energy conversion and storage.

Conflict of Interests

The authors declare no interest conflict.

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Graphical Abstract

Toward High-crystalline Covalent Organic Framework *via* Dynamic Condensation of Carbon-Carbon Double Bond

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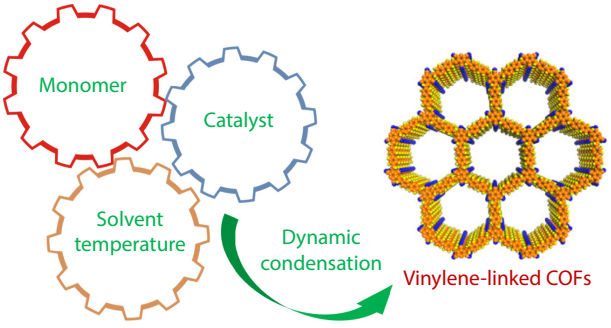
Shanghai Jiao Tong University; Yunnan Advanced Elastomer Industry Innovation Research Institute Co., Ltd.

This review outlines recent advances in the Knoevenagel/aldol condensation approach to build up high-crystalline two-dimensional dynamic vinylene-linked covalent organic frameworks promoted by monomer design and reaction condition optimization.



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