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Chemical conversion and locking of the imine linkage: enhancing the functionality of covalent organic frameworks

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Abstract: Imine-based covalent organic frameworks (COFs) are a widely studied class of functional, crystalline, and porous nanostructures which combine a relatively facile crystallization with tuneable compositions and porosities. However, the imine linkage constitutes an intrinsic limitation due to its reduced stability in harsh chemical conditions and its unsuitability for in-plane π -conjugation in COFs. Urgent solutions are therefore required in order to exploit the full potential of these materials, thereby enabling their technological application in electronics, sensing and energy storage devices. In this context, the advent of a new generation of linkages derived from the chemical conversion and locking of the imine bond represents a cornerstone for the synthesis of new COFs. A marked increase in the framework robustness is in fact often combined with the incorporation of novel functionalities including, for some of these reactions, an extension of the in-plane π -conjugation. This Minireview describes the most enlightening examples of one-pot reactions and post-synthetic modifications towards the chemical locking of the imine bond in COFs.

1. Introduction

Covalent organic frameworks (COFs) are artificial crystalline porous nanostructures based on light elements (C, H, O, N, Si) interconnected by covalent bonds. Over the past 15 years, COFs have attracted great attention because of their unique physicochemical properties which rendered them powerful materials for potential applications in gas storage, molecular separations, photo/electrocatalysis, electronics, sensing, energy storage, etc.^[1]

Prior to the development of dynamic covalent chemistry (DCC)^[2] it was believed that such covalently linked crystalline solids could not be produced by means of conventional *bottom-up* wet approaches. In 2005, Yaghi and co-workers reported the first solution to overcome this impasse, by connecting rigid aromatic building-blocks with highly reversible boroxine and boronate ester rings.^[3]

Ever since, a series of other reactions have been applied for the reticulation of COFs such as the Schiff base reaction (imine,^[4] hydrazone^[5] and azine formation^[6]), the triazine formation,^[7] the imide condensation,^[8] and the Knoevenagel condensation.^[9] In general, the topology of COFs derives from the rigidity and geometry of the building-blocks. Towards this end, most molecular units employed for the COFs synthesis exhibit extended aromaticity, which results in a strong contribution of the π - π stacking interaction as driving force in the crystallization process. Therefore, the majority of the reported COFs consists of 2D layered structures, albeit remarkable examples of 3D COFs have also been described.^[4, 10] Regardless the chemistry used, a high degree of crystallinity can only emerge when the covalent connection is established under thermodynamic control, which can ensure the microscopic reversibility of the reaction, providing a dynamic error correction. The formation of long-range crystalline phases is thus typically achieved by solvothermal

methods, which entail a closed system, high temperatures, and often the presence of specific catalysts.^[11]

As much as the reversibility of the covalent linkage is essential to achieve enhanced crystallinity, it is also accompanied by inherent limitations in terms of chemical stability of the material, resulting in an apparent persistent trade-off between crystallinity and robustness. Dynamic imine chemistry, which operates under relatively mild thermodynamic and catalytic conditions, represents a good compromise between these two aspects and in the past years it has become the most employed method for the construction of 2D and 3D COFs outclassing boroxine and boronate ester COFs. While weak nucleophiles such as water, even in the form of moisture in the air, can potentially hydrolyse the B-O bond,^[12] they are more harmless to imine COFs, the latter being less prone to undergo decomposition under such conditions.^[13]

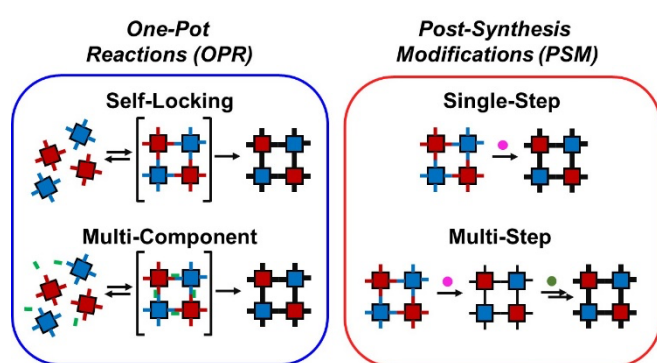
Nevertheless, the stability of imine COFs is challenged when operating in harsh conditions such as the presence of strong acids, bases, or redox agents.^[14] Alongside, it has been shown that imine-linked 2D COFs are generally less thermally stable than their boronate ester-linked counterparts.^[15] As a consequence, these materials are still premature for industrial applications such as catalysis, gas storage or gas separation, etc. for which the exposure to a range of reactive species and severe physical conditions is envisaged, demanding for a superior chemical and thermal robustness.^[16]

Additionally, a great deal of attention is currently paid to 2D π -conjugated COFs as they appear ideal for applications in electronic and electrochemical energy devices.^[17] Indeed, theoretical studies predict semiconducting properties with highly tuneable band gaps and strict correlation between topology and electronic properties in these materials.^[18] Nevertheless, even when (photo)electroactive units, such as porphyrins, pyrenes, thiophenes, and phthalocyanines are embedded into the COF structure, 2D imine COFs exhibit limited in-plane π -conjugation due to the inherent polarization of the C=N connection.^[9, 19] The resulting (photo)conductive properties are therefore highly anisotropic and mainly dependent on the vertical stacking of the (photo)electroactive units which creates large π -orbital overlap, thus charge delocalization along the out-of-plane direction.^[20]

In recent years, a few approaches have been devised to overcome imine COFs' stability drawbacks.^[16a, 21] The nucleophilicity of the C=N bond could be decreased moving to the hydrazone or azine linkages.^[5-6] Alternatively, improving the interlayer interaction in 2D imine COFs was demonstrated to be beneficial for generating multi-layered materials with superior stability. This could be achieved with various approaches such as intramolecular hydrogen-bonding,^[22] molecular docking,^[23] interlayer hydrogen-bonding,^[24] and resonance stabilization.^[25] However, these methods only partially reduce the intrinsic dynamic nature of the C=N bond and fail in addressing the enhancement of the in-plane π -conjugation between the aromatic building-blocks. Tackling these issues is strongly desired for the

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next generation of COFs and in particular for the fabrication of COFs-based thin films, which are regarded as more promising than the bulk materials for several advanced applications.^[26] Interestingly, some recent works highlighted the possibility of performing a reversible – irreversible covalent reaction sequence based on the dynamic imine chemistry as reversible step, yielding in new linkages that could not be easily obtained following other synthetic paths. This locking approach pledges to achieve kinetically blocked and chemically robust COFs while maintaining accessible reaction conditions and preserving the high crystallinity of the material, typical of the covalent dynamic linkages. Furthermore, a careful choice of the synthetic strategies can enhance the in-plane π -conjugation and/or introduce additional functionalities conferring new physicochemical properties to the resulting COFs.



Scheme 1. Formation of robust COFs by irreversibly locking the imine bond: one-pot reactions (self-locking and multi-component) and post-synthesis modifications (single- and multi-step).

To date the proposed strategies for the chemical locking of the imine linkage can be divided in two fundamentally different categories, *i.e.* one-pot reactions^[16a] and post-synthesis modifications (Scheme 1).^[27] Within one-pot reactions (OPRs) the formation of the irreversible bond is accomplished through a sequence of reactions that occur directly during the crystallization process. The first step of the sequence is necessarily involving the imine formation under thermodynamic control, which provides the *error-checking* and *self-correcting* capabilities to the system. A subsequent irreversible reaction, occurring *in situ*, locks the C=N connection. In this context, self-locking linkages can be implemented by pre-designing the monomers with appropriate functional groups programmed to undergo a second reaction once the imine bond is formed. Alternatively, by making use of a multi-component approach, the locking reaction can be triggered by a third component present in the reaction mixture that gets integrated into the structure of the linkage.

While OPR steps are often entangled, thereby jeopardizing the material crystallinity, the use of a post-synthesis modification (PSM) approach makes it possible to completely decouple the reversible imine formation and locking reaction. By mastering this method, an imine crystalline polymer is firstly synthesized and isolated in a conventional way. Only successively the C=N linkage is chemically converted into more functional and robust moieties *via* a solid-state modification reaction. In some cases, multi-step synthetic modifications have been described, allowing to introduce complex functionalities into the linkages and tailor the pores of the frameworks.

While the exploitation of a wide range of well-known organic chemistry reactions has boosted the development of COFs based

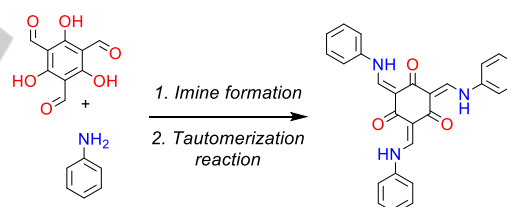
on the chemically modified C=N connection, many synthetic strategies are yet to be explored. This evolution has the potential to expand the plethora of possible COF applications, overcoming some of the limits of imine-based materials. In this Minireview article we will showcase and rationalize the advances in the field of chemical locking of the imine linkage to generate highly stable COFs with extended π -conjugation and/or additional functionalities. We expect that a comprehensive view of the tools available may help to stimulate further research efforts in this direction with the ultimate goal of achieving a deeper control over the physicochemical properties of COFs. We firstly introduce the main strategies for OPRs divided into self-locking and multi-component OPRs, followed by a section dedicated to the single-step and multi-step PSMs, to finally conclude with a comparison between the methods and some outlooks.

2. One-Pot Reactions

2.1. Self-Locking OPRs

As previously discussed, in a COF the amine or the aldehyde building-blocks can be specifically pre-modified to carry out a locking reaction sequence in a subsequent fashion, referred to as self-locking OPRs. The combination of reactions starts with the imine formation under thermodynamic control, followed by an irreversible tautomerization or cyclization, typically triggered by the presence of reactive functional groups in the *ortho*-position of one or both the monomers (Scheme 2).

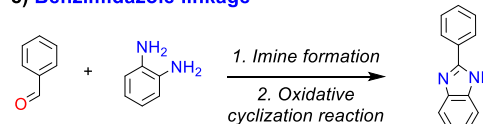
a) -ketoenamine linkage



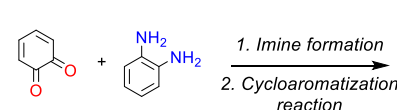
b) Benzoxazole linkage



c) Benzimidazole linkage



d) Phenazine linkage



Scheme 2. Different types of reversible – irreversible sequences used for the construction of COFs by self-locking OPRs.

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In their seminal work in 2012, Banerjee and co-workers reported the first example of reaction sequence, proposing a method for the synthesis of β -ketoenamine-linked COFs (Scheme 2a). By reacting linear diamine linkers, such as 1,4-phenylenediamine (PDA), with the hydroxylated reagent 1,3,5-triformylphloroglucinol (Tp) as tritopic knot in place of the geometrically equivalent 1,3,5-triformylbenzene (TFB), the authors observed the formation of the new linkage.^[28] The synthesis of TpPa-1 was carried out under standard solvothermal conditions (*i.e.* 120 °C for 3 days) with a mesitylene/dioxane solvent mixture and in the presence of 3 M acetic acid as catalyst. The reaction initiates with the aldehyde – amine reversible condensation according to the Schiff base reaction, promoting the formation of a long-range ordered structure. Subsequently, a quantitative irreversible proton tautomerization ensures the locking of the carbon-nitrogen bond switching from the enol – imine to the keto – enamine form (Figure 1). Noteworthy, upon the transformation of the imine to β -ketoenamine the crystallinity and pore properties of the material were maintained. The powder material exhibited thermal stability up to 350 °C, superior chemical resistance proved by the crystallinity retention after the exposure to boiling water and acid environment (9 M HCl) up to 7 days. However, unless bulky methyl groups ($-\text{CH}_3$) were positioned near the nitrogen centre (TpPa-2), significant loss of crystallinity, surface area and weight were evidenced after one day under strong alkaline conditions (9 M NaOH) possibly associated with the backward keto-to-enol reaction.

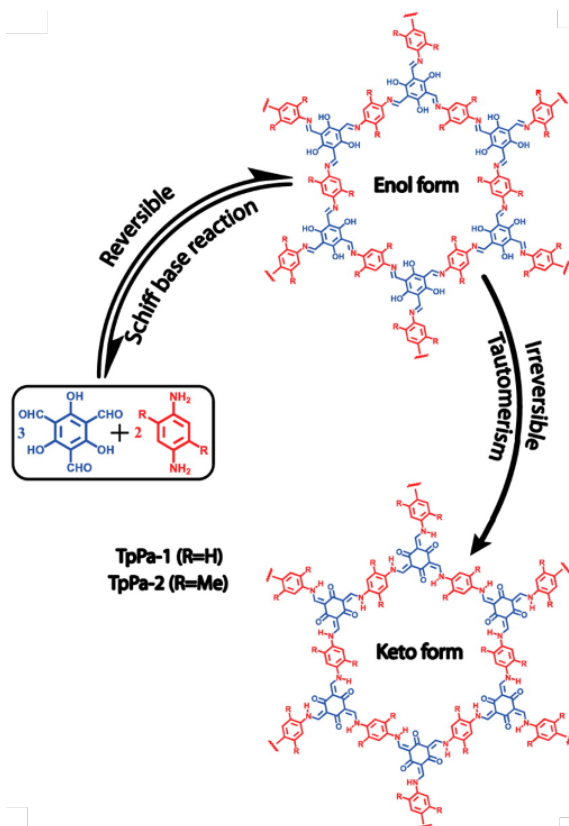


Figure 1. Reversible – irreversible reaction sequence between triformylphloroglucinol with p-phenylenediamine and 2,5-dimethyl-p-phenylenediamine to form TpPa-1 and TpPa-2 respectively. Adapted with permission from ref. 28, Copyright American Chemical Society.

Ever since its development, the β -ketoenamine OPR strategy has become one of the most used methods to easily prepare highly stable 2D COFs. Noteworthy, it has also been shown that this linkage can be employed for the reticulation of 3D frameworks.^[29] Moreover, thanks to the adaptability of the reaction conditions, this chemistry has been exported from classical solvothermal synthesis to the greener synthesis in water,^[30] mechanochemical synthesis,^[31] interfacial synthesis,^[32] knife-casting and baking,^[33] and 3D printing of self-supported COF foams.^[34]

When the amine building-block is functionalized in the *ortho*-position with a nucleophilic group such as $-\text{OH}$, $-\text{SH}$ or $-\text{NH}_2$, the reaction sequence comprising imine formation – oxidative cyclization can be easily triggered in presence of an oxidant, resulting in organic frameworks interconnected by benzoxazole rings. However, for many years the entangled nature of this reversible – irreversible reaction pair has been difficult to disentangle, consistently leading to the rapid and irreversible formation of the polymers by oxidative cyclization before the self-correcting process could generate long-range positional order in the structure. The resulting amorphous microporous polymers based on benzoxazole,^[35] benzothiazole,^[36] and benzimidazole^[37] linkages were reported. Great synthetic efforts have been devoted to build crystalline materials. Hitherto, a few different methods have been proposed for the preparation of benzoxazole and benzimidazole-linked COFs, while the self-locking OPR version of the benzothiazole remains to be addressed.

Three ultrastable benzoxazole-linked COFs were synthesized under solvothermal conditions by Wang and co-workers (Scheme 2b).^[38] After an extensive screening it was found that N-methyl-2-pyrrolidone (NMP)/mesitylene mixed solvents and a benzimidazole additive at 185 °C were the optimal conditions for the crystallization. Three different aldehydes were reacted with 2,5-diamino-1,4-benzenediol (DABD) affording the COFs LZU-190, LZU-191, and LZU-192 (Figure 2a). The presence of the benzimidazole additive turned out to be crucial for its role as dehydrogenation and templating agent, yielding to high quality crystalline materials with Brunauer–Emmett–Teller (BET) surface areas that were estimated amounting to 1035, 1305, and 706 $\text{m}^2 \text{g}^{-1}$, respectively. High structural stability was demonstrated up to 400 °C and upon 3 days treatments in boiling water, pure trifluoroacetic acid (TFA), 9 M HCl and 9 M NaOH after which non change in the powder X-ray diffraction (PXRD) spectra was evidenced (Figure 2b). Moreover, the reticulation of oxazole-linked COFs widely extends the in-plane π -conjugation, thereby decreasing the optical bandgaps (measured as 2.02, 2.38, and 2.10 eV, respectively) and greatly enhancing their visible light absorption (Figure 2c). By taking advantage of their ultrahigh stability and photophysical properties the authors demonstrated the applicability of such materials for the photocatalysis of the oxidative hydroxylation of arylboronic acids to phenols.

Alongside, it is worth highlighting the fundamentally different synthetic approach based on cyanide catalysis adopted by McGrier and co-workers.^[39] Benzoxazole-linked LZU-190, LZU-192 and BBO-2 were produced by reacting DABD with three aldehydic knots. To ensure the slow formation of the intermediate imine-linked network and avoid the prompt precipitation, the reactants were mixed in dimethylformamide (DMF) at -15 °C for 3 h before warming the mixture to room temperature and adding the NaCN. Subsequent treatment at 130 °C for 4 days in presence of air resulted in the formation of the three benzoxazole-linked COFs. The NaCN catalysis was demonstrated to stabilize the radical

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intermediates that are formed during the oxidative dehydrogenation step of the oxazole ring formation in air.^[39b] It was also observed that the inclusion of an electron deficient moiety in the amine monomer such as triazine in LZU-191 not only aids in increasing the crystallinity of the materials by promoting the formation of donor – acceptor stacking layers, but also takes part in the delocalization of radicals generated during the oxidative dehydrogenation process. While both the BET surface area and the crystallinity of LZU-190 ($891 \text{ m}^2 \text{ g}^{-1}$) were slightly lower compared to the same COF produced by the previous method,^[38] a noticeable improvement from 1305 to $2039 \text{ m}^2 \text{ g}^{-1}$ was observed for LZU-191.

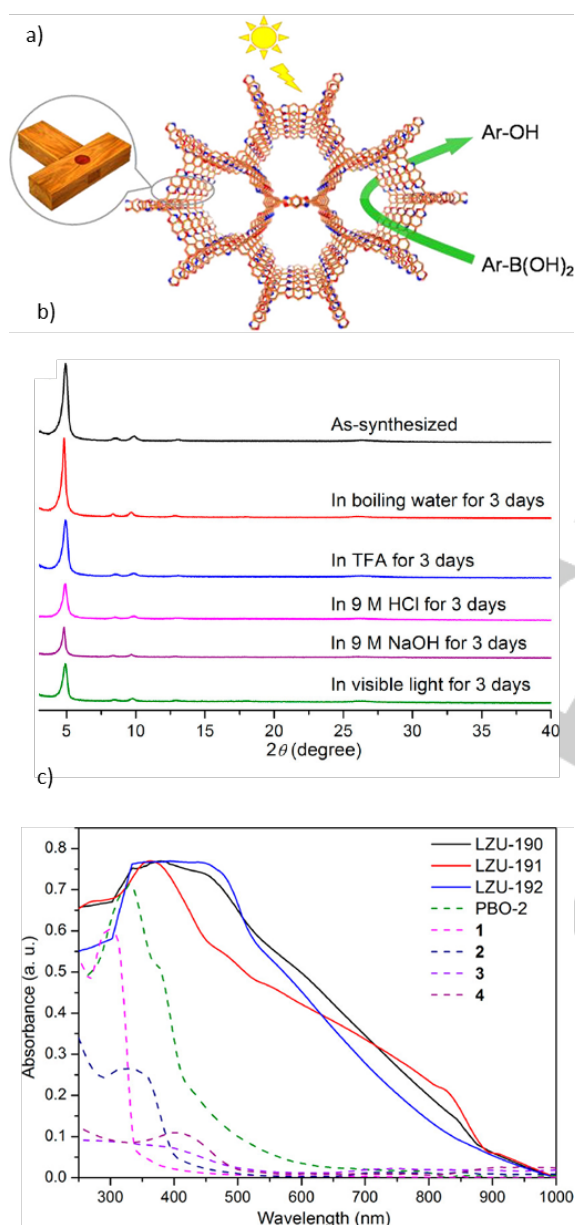


Figure 2. (a) Schematic illustration of the photocatalytic oxidative hydroxylation of arylboronic acids to phenols. (b) PXRD patterns measured after 3 day treatment of LZU-190 in different aggressive media. (c) UV-vis absorption spectra of LZU-190, LZU-191, and LZU-192, compared with the model compound PBO-2, and their building-blocks (dashed lines). Adapted with permission from ref. 38, Copyright American Chemical Society.

A benzimidazole-linked COF was more recently prepared by Mandal and co-workers by reaction between a tritopic aldehydic knot and 1,2,4,5-tetramino-benzene (TAB) linker, using reaction conditions similar to those used by Wang (Scheme 2c).^[40] The synthesis was performed in mesitylene/NMP/dioxane at $120 \text{ }^\circ\text{C}$ and using imidazole as dehydrogenation agent. The high thermal ($400 \text{ }^\circ\text{C}$) and chemical stability (3 M NaOH and 3 M HCl for 7 days) combined with the elevated BET surface area (up to $1424 \text{ m}^2 \text{ g}^{-1}$) and the heteroatoms present in the skeleton made this material suitable for applications in gas and liquid capture and separation.

Beside the formation of 5-membered heteroaromatic rings, the phenazine OPR relies on a sequence of two consecutive imine condensations of an α -diketone with an α -diamine, achieving 2D aza-fused COFs which are linked by 6-membered rings (Scheme 2d). While the first step is reversible, the second has an irreversible nature due to the additional stabilization of the aromatic product. In 2013, Jiang and co-workers reported the phenazine-linked CS-COF formed *via* double imine condensation between triphenylene hexamine (TPHA) and *tert*-butylpyrene tetraone (PT).^[41] Ethylene glycol was used as solvent and catalytic 3 M aqueous acetic acid was added under standard solvothermal conditions, with the *tert*-butyl side groups in PT being employed to enhance the solubility of the otherwise insoluble building blocks. The resulting CS-COF framework was chemically stable in both acidic (1 M HCl) and basic (1 M NaOH) environments up to 24 h. The high conjugation expressed by the phenazine linkage extends the π -delocalization over the whole sheet of COF and renders this material appealing for its electronic properties. CS-COF is a high-rate hole-conducting framework with an exceptional mobility of $4.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

More recent works reported a further improvement in the electronic properties of the material, comprising electroactive phthalocyanine knots in the structure. The highly conjugated phthalocyanine-based, phenazine-linked COF-DC-8,^[42] ZnPc-pz and CuPc-pz^[43] (Figure 3a) were obtained from the condensation reaction between a PT moiety and the octa-amino derived phthalocyanine (MOAPc, M = Ni, Zn, Cu). The fully aromatic and crystalline 2D COFs (Figure 3b) showed excellent chemical and thermal stability and interesting electronic properties. The intrinsic bulk conductivity of COF DC-8 was measured as high as $2.51 \times 10^{-3} \text{ S m}^{-1}$ and could be further increased of three orders of magnitude upon iodine doping. ZnPc-pz and CuPc-pz are p-type semiconductors with a record hole mobility of $5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an intrinsic conductivity of $5 \times 10^{-7} \text{ S m}^{-1}$. DFT calculations carried out independently by the two groups suggest that the charge transport in these materials may be anisotropic with a predominant conduction along the *c*-axis and a negligible in-plane contribution. Unfortunately, due to the polycrystallinity (Figure 3c) of the materials, the results of these calculations could not be confirmed experimentally.

The electrical properties along the in-plane direction of a phenazine-linked 2D COF were studied experimentally by the groups of Choi and Kim suggesting a different behaviour compared to the aforementioned DFT predictions.^[44] In the first work the authors proposed a light-driven method for the preparation of an atomically thin film of a highly conjugated and crystalline COF (hcc-COF). The charge transport properties were studied by integrating the hcc-COF film as active component in a field-effect transistor (FET)-type device. Owing to its highly π -conjugated structure along the in-plane direction, the obtained 2D

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films displayed remarkable semiconducting properties with a state-of-the-art electrical conductivity of 0.40 S m^{-1} . Indeed, this value is two orders in magnitude higher than that of the corresponding bulk material ($2.22 \times 10^{-3} \text{ S m}^{-1}$) and the imine-linked pi-COF thin film ($5.51 \times 10^{-3} \text{ S m}^{-1}$) produced through the same method.

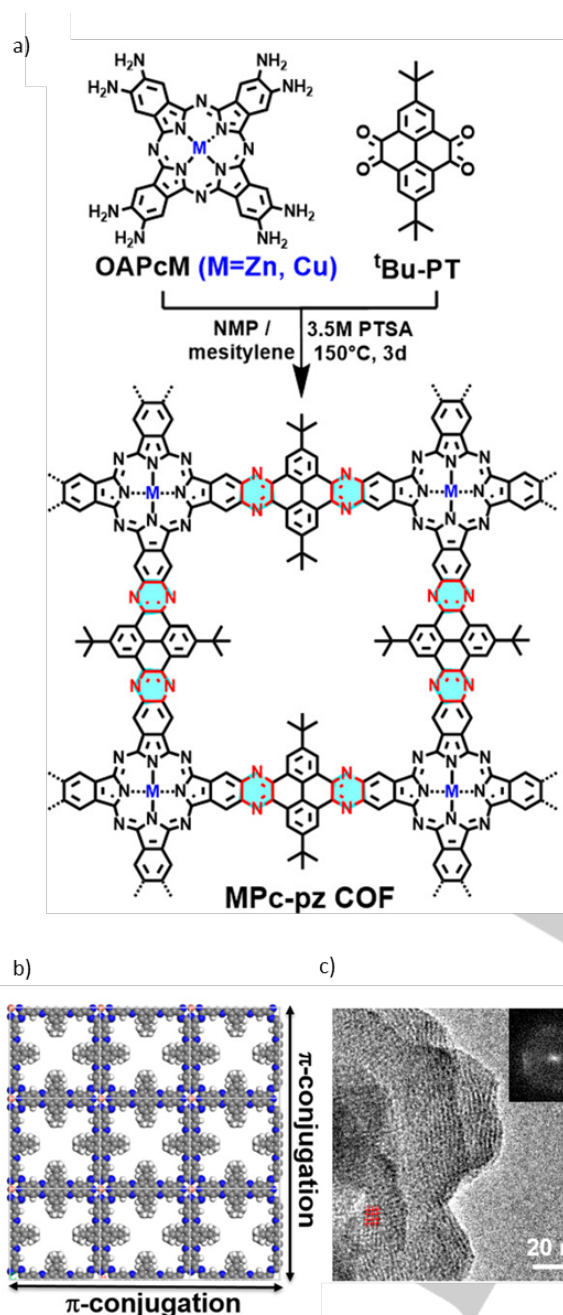


Figure 3. (a) Reaction scheme for the synthesis of MPC-pz COF (M = Zn or Cu). (b) Top view and conjugation paths of a monolayer of MPC-pz. (c) high resolution-TEM image of ZnPc-pz including the Fourier transform (FFT) analysis. Adapted with permission from ref. 43, Copyright American Chemical Society.

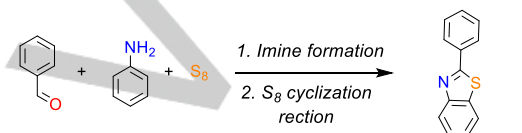
Furthermore, Kim and co-workers recently reported the preparation of a solution-processable phenazine-linked COF, by reacting 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and 2,3,6,7,10,11-hexaaminotriphenylene (HATP) in an oxygenated environment.^[45] Interestingly, the reaction is believed to occur by

autoxidation of HHTP to quinone and semiquinone species, which further react by double condensation with the diamine monomers.^[46] FET devices based on 2.5 nm thick layers of this material generated high hole mobilities, up to $4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and conductivity values up to 1.75 S cm^{-1} .

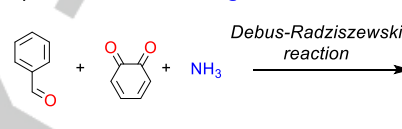
2.2. Multi-Component OPRs

The locking approach can also be exploited through a multi-component reaction (Scheme 3). According to this method, in addition to the classical Schiff base reagents, a third component added to the reaction mixture is integrated in the chemical structure of the linkage. In analogy to the self-locking OPRs, these reactions combine the reversibility of the imine formation that provides the long-range ordered structure, with a subsequent irreversible step that imparts stability.

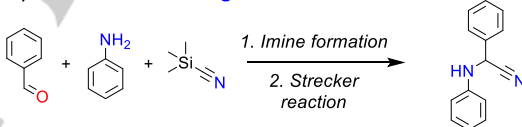
a) Benzothiazole linkage



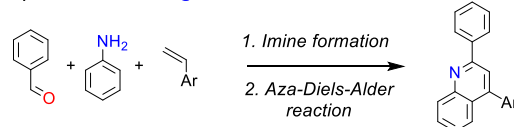
b) Benzimidazole linkage



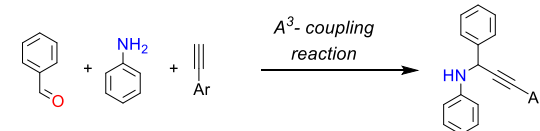
c) -aminonitrile linkage



d) Quinoline linkage



e) Propargylamine linkage



Scheme 3. Different types of reversible – irreversible sequences used for the construction of COFs by multi-component OPRs.

Benzothiazole-linked COF can be constructed by multi-component OPR. Very recently Cooper and co-workers proposed the direct reaction between the amine and aldehydes building blocks with elemental sulfur as viable route to produce a series of new 2D layered COFs named TZ-COFs (Scheme 3a).^[47] The reactions were conducted in standard solvothermal conditions, in a mixture of solvents with 6 M acetic acid as catalyst and dimethyl sulfoxide (DMSO) as oxidant. The proposed mechanism involves the formation of imine bond followed by the electrophilic attack of sulfur to the amine *ortho* position and consecutive oxidative aromatization by DMSO. The reversibility of the imine

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condensation combined with the irreversibility of the sulfur cyclization yielded a material exhibiting both high crystallinity and BET surface area ($1705 \text{ m}^2 \text{ g}^{-1}$ for TZ-COF-4) combined with superior thermal (up to $450 \text{ }^\circ\text{C}$) and chemical stability (tested in concentrated strong acids and bases as well as reductants). The photocatalytic applications of the TZ-COFs were investigated, and TZ-COF-4 gave high sacrificial hydrogen evolution rates from water (up to $4296 \mu\text{mol h}^{-1} \text{ g}^{-1}$ under visible light irradiation) coupled with high stability and recyclability.

Interestingly, a multi-component OPR route to benzimidazole-linked COFs was reported very recently by Wang et al. via Debus–Radziszewski reaction (Scheme 3b).^[48] The reaction, portrayed in Figure 4, does not proceed through the classical aromatic amine – aromatic aldehyde condensation but rather through three-components condensation between PT, ammonium acetate, and aldehydes. While the exact mechanism of the linkage formation has not been yet clearly demonstrated, it is speculated that the OPR proceeds through an initial geminal bis-imine formation between the aldehyde monomer and ammonium acetate followed by cycloaromatization with the dicarbonyl building-block with the loss of two molecules of water. These COFs exhibit only modest crystallinity and surface area most likely due to the limited reversibility of the imidazole formation. On the other hand, the high stability was demonstrated by 3 days exposure to aqueous NaOH (9 M) and HCl (9 M) and the frameworks could be further post-modified by *N*-alkylation of the imidazole rings with alkyl bromides.

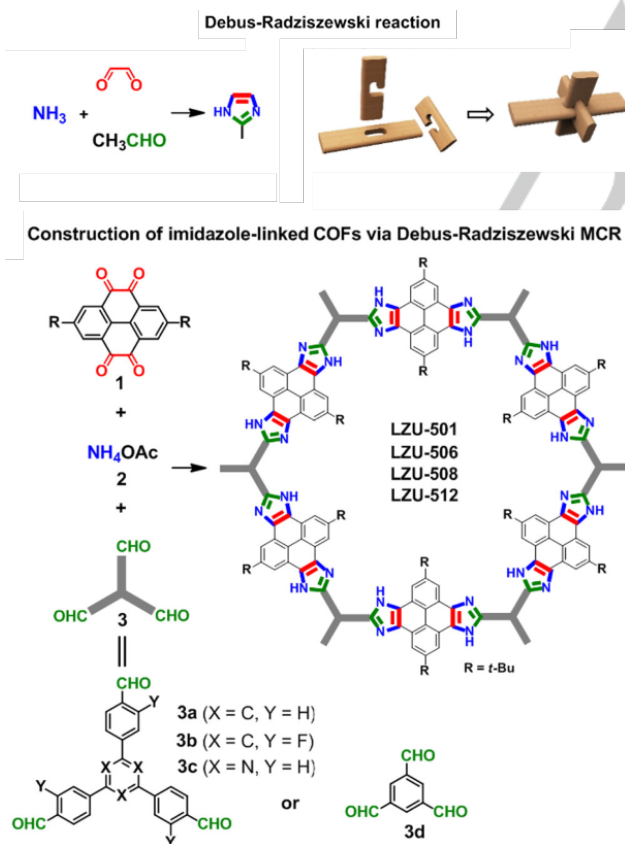


Figure 4. (a) Schematic representation of the multi-component Debus–Radziszewski reaction. (b) Reaction scheme for the synthesis of LZU-501, 506, 508, 512. Adapted with permission from ref. 48, Copyright American Chemical Society.

A strategy to convert the reversible C=N double bond in a single C-N bond involves the application of the Strecker reaction to the COF synthesis (Scheme 3c). This reaction has been commonly employed for the preparation of α -aminoacids^[49] and can easily be adapted for the preparation of α -aminonitrile compounds starting from the respective imines.^[50] A multi-component OPR version of the Strecker synthesis was developed to form stable α -aminonitrile-linked COFs.^[51] The three-component reaction was carried out by dissolving the amine and the aldehyde building-blocks with trimethylsilyl cyanide (TMSCN) in 1,2-dichlorobenzene (*o*-DCB)/1-butanol (*n*-BuOH) mixture and using standard solvothermal conditions with the assistance of acetic acid and $\text{BF}_3 \cdot \text{OEt}_2$. The resulting α -aminonitrile-linked S-TmTaDm-COF and other COFs were synthesized with this method demonstrating its general applicability. The BET surface area ($1405 \text{ m}^2 \text{ g}^{-1}$) decreased compared to the relative imine-linked TPB-DMTP-COF ($2105 \text{ m}^2 \text{ g}^{-1}$) as a result of the increase in the framework mass and the slight reduction in crystallinity.^[25] Additionally, the stability comparison revealed that the α -aminonitrile-linked material possess higher stability in oxidizing medium (1 M KMnO_4) while the imine structure was found superior in basic (14 M NaOH) and reducing (1 M NaBH_4) media. Despite no substantial stability improvement, the success of this multi-component strategy and the possibility of adding pendant functionalities such as nitrile groups at the linkage remain an important achievement in the field of imine COF modifications.

More promising for the improved stability and conjugation of the products is the aza-Diels–Alder reaction that has been applied as successful method to convert *in situ* the reversible C=N linkage into a robust quinoline moiety (Scheme 3d).^[51] As an example, the three-component reaction could be performed by dissolving the knot 3,5-tri(4-aminophenyl)benzene (TAPB) and the linker 2,5-dimethoxy terephthalaldehyde (DMTPA) with styrene in a mixed solvent system of *o*-DCB/*n*-BuOH under standard solvothermal conditions in presence of $\text{BF}_3 \cdot \text{OEt}_2$, chloranil and acetic acid. The obtained P-StTaDm-COF exhibited high crystallinity and improved chemical stability in acidic environment (12 M HCl).

By employing a multi-component OPR, known as A^3 -coupling reaction (aldehyde-alkyne-amine), the chiral propargylamine-linked (S)-DTP-COF was prepared by Dong and co-workers (Scheme 3e).^[52] The polymerization took place at room temperature in chloroform in the presence of the chiral (S,S) pyridine-2,6-bis(oxzoline)-Cu(I) complex, employed as the catalyst. Circular dichroism (CD) experiments confirmed the chirality of the framework and, as expected, by using the (R,R) enantiomer of the catalyst the specular (R)-DTP-COF was generated by the same reaction. (S)-DTP-COF is a crystalline solid with a BET surface area of $684 \text{ m}^2 \text{ g}^{-1}$, which also showed high chemical robustness toward many organic solvents as well as 12 M NaOH, 2 M HCl and thermal stability up to $300 \text{ }^\circ\text{C}$. The obtained chiral framework was applied as chiral catalysts to promote asymmetric Michael addition reactions.

3. Post-synthesis Modifications

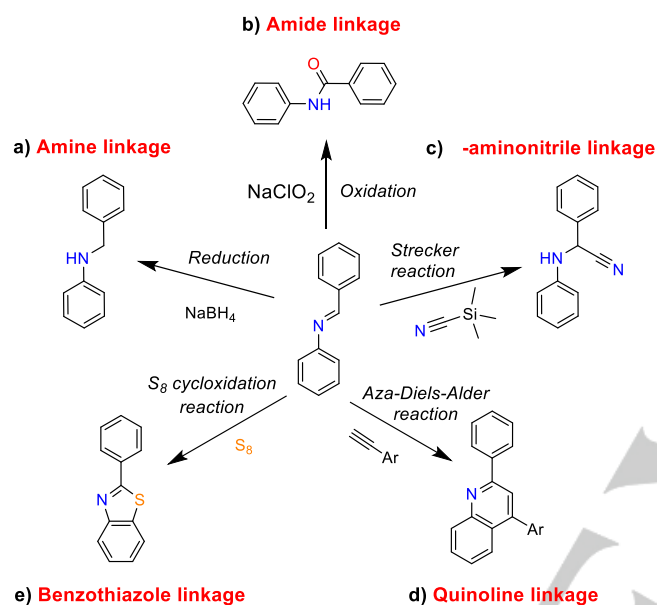
The ordered and porous nature of the COFs structures represent two among the most interesting characteristics of these materials. The high surface area exposed enables reactive chemical species to diffuse inside the material's pores and virtually reach all the organic moieties of the structure. Taking advantage of this

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feature a series of PSM of the linkage have been developed. PSM is a versatile strategy that allows transforming the linkage of a pre-synthesized imine COF into more functional moieties including benzoxazoles, quinolines amides and others, by means of various single-step or multi-step solid-state reactions.

3.1. Single-Step PSMs

The imine C=N bond can be oxidized directly to amide or reduced to secondary amine, when treated with suitable redox agents. The solution redox chemistry of the C=N bond has been transferred to solid-state synthesis achieving the kinetically locked amine and amide-linked COFs.



Scheme 4. Different types of irreversible reactions used to lock the imine-bond in COFs by PSMs.

The irreversible reduction of the imine bond to a secondary amine group was reported by Deng and co-workers in 2018 both for 2D and 3D imine COFs (Scheme 4a).^[53] The successful quantitative conversion was obtained by PSM reaction of COF-300 and COF-366-M (M = Cu, Co or Zn) with the reducing agent NaBH₄ in methanol in presence of terephthalic acid (TPAc) at -10 °C. Minor changes in the lattice parameters were evidenced by PXRD when moving from the imine to the amine-linked structure and they were associated with conversion of the carbon hybridization from sp² to sp³. In general, it was found that the underlying topology was unaltered. The single C-N bond of the secondary amine loses the microscopic reversibility characteristic of the C=N bond thus locking the linkage. The improved chemical stability of the modified COF compared to the pristine material was demonstrated by exposing the samples to aqueous solutions at low (6 M HCl) and high (6 M NaOH) pH for 12 h. The amine COFs maintained their crystallinity after the treatments while the unmodified materials partially lost their structure in NaOH and completely dissolve in HCl. Coupled with other materials, amine-linked COFs were conveniently applied in catalysis and electrocatalysis, with the function of structural scaffolds and adsorption site for the reactant molecules.^[53-54]

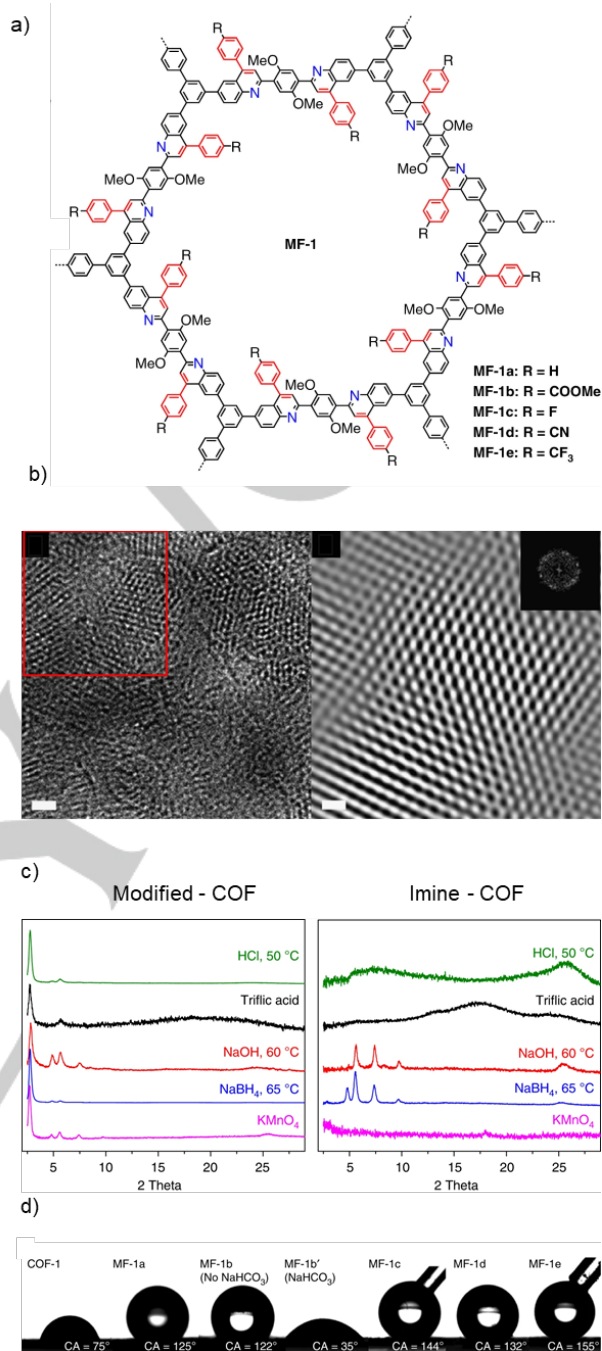


Figure 5. (a) Structure of MF-1. (b) (left) Low-dose, high resolution TEM image of MF-1a, scalebar 10 nm and (right). Fourier-filtered image of the selected red square area, scalebar 5 nm (c) Chemical stability tests of the MF-1a and COF-1. (d) Water contact angles of water droplet on the pressed pellet of COF-1 and MF-1a-e. MF-1b' is the NaHCO₃-treated MF-1b that undergoes partial ester hydrolysis. Adapted with permission from ref. 14, Copyright Springer Nature.

Yaghi and co-workers transformed two layered imine-linked COFs (TPB-TP-COF and 4PE-1P-COF) in the corresponding, isostructural amide-linked COFs by direct oxidation of the C=N in mild conditions (Scheme 4b).^[55] The reaction was carried out at room temperature using an excess of sodium chlorite (NaClO₂) as oxidizing agent in presence of acetic acid in dioxane for 48 h. The addition of an olefin scavenger such as 2-methyl-2-butene (scavenger of hypochlorous acid generated as a by-product of the

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reduction of chlorite) further improved the crystallinity of the final material. The chemical stability of the pristine imine COFs was compared with that of the modified amide COFs by treatment for 24 h in 12 M HCl and 1 M NaOH. The amide COFs demonstrated much higher retention of crystallinity, especially in the case of exposure to acidic conditions, confirming the higher kinetical stability of the bond. Interestingly, the same reaction protocol was more recently employed by Cui *et. al.* to prepare a 3D chiral COF from the reticulation of a tetrahedral tetraamine with a chiral enantiopure tetraaldehyde, followed by PSM – oxidation of the linkage with NaClO₂.^[56] The resulting highly stable amide-linked COF was used as chiral stationary phases for high performance liquid chromatography (HPLC) to separate racemic mixtures.

Very recently, Dong and co-workers performed the Strecker synthesis in its solid-state version to modify the imine-linked TPB-DMTP-COF (Scheme 4c).^[51] The PSM reaction was carried out using TMSCN as cyanide ion source and BF₃·OEt₂ in toluene in standard solvothermal conditions. Compared with the corresponding framework obtained by the OPR route, the PSM method features an α -aminonitrile-linked COF with the same structure but slightly lower degree of crystallinity.

As discussed in the previous section, upon reaction with aryl alkynes or aryl alkynes, the imine linkages in COFs can be converted to yield the corresponding quinoline-linked COFs which features an extended π -electron delocalization.^[14, 51, 57] The reaction is relatively versatile and could be carried out both in its OPR and its PSM versions. The PSM of the pre-synthesized imine COF-1 (Figure 5a) was achieved for the first time by using phenylacetylene at 110 °C in the presence of BF₃·Et₂O and chloranil in toluene for 3 days (Scheme 4d).^[14] The material showed high crystallinity (Figure 5b) and despite the limited conversions of 20 – 30%, the stability upon exposure to aggressive chemicals was substantially enhanced (Figure 5c). A large variety of functional moieties could be introduced in the *para*-position of the phenylacetylene yielding to the series MF-1a-e. Bearing groups such as fluorine, nitrile and trifluoromethyl on the pore surfaces resulted in a selectively altered wettability of the material (Figure 5d). Noteworthy, the improvement of the π -delocalization resulted in a reduced optical bandgap of the modified materials (2.30 eV for MF-1a) compared to that of the imine COF-1 (2.52 eV).

In a remarkable work by Lotsch and co-workers, two pre-synthesized imine COFs (TTI-COF and PBI-COF) were modified by reaction with elemental sulfur achieving the correspondent benzothiazole-linked COFs TTT-COF (Figure 6a) and PBT-COF (Scheme 4e).^[58] The molten reactant was infiltrated in the COF at 155 °C, temperature at which it has reduced viscosity. Subsequently the temperature of the mixture was raised to 350 °C resulting in the linkage conversion from imine to benzothiazole. The proposed mechanism involves the nucleophilic attack of the elemental sulfur to the imine carbon to form an intermediate thioamide group followed by oxidative cyclization to thiazole ring at the expense of the reduction of elemental sulfur to H₂S. The improved stability of the modified TTT-COF was tested and compared to the pristine TTI-COF by exposing the materials for 16 h to 12 M HCl (50 °C), 12 M KOH, 1 M hydrazine and 1M NaBH₄. In all the cases the benzothiazole COFs remained unaffected, while the correspondent imine COF lost its crystallinity in all the conditions except showing some resistance only to HCl (Figure 6c). Moreover, the incorporation of sulfur atoms in the COF backbone in the form of benzothiazole endowed the material

enhanced endurance to the high energy transmission electron microscopy (TEM) electron-beam together with improved contrast that allowed the authors to obtain high-quality images and study the structural defects of the material such as grain boundaries formed earlier during the crystallization of the imine COF (Figure 6b).

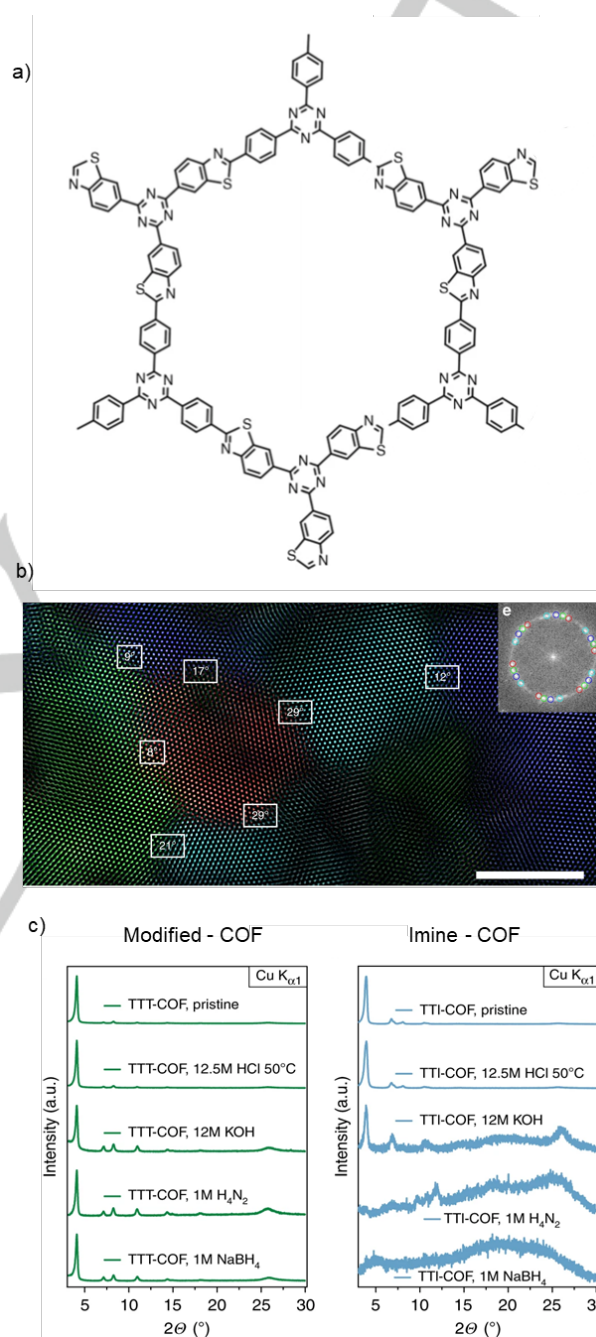


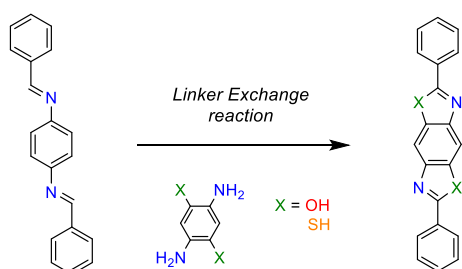
Figure 6. (a) Structure of TTT-COF. (b) high resolution TEM image of TTT-COF, scalebar 50 nm. The colors distinguish the different crystalline domains. (c) Chemical stability tests of the TTT- and TTI-COFs evaluated by recording the PXRD spectra after the exposure to aggressive chemicals. Adapted with permission from ref. 58, Copyright Springer Nature.

Post-synthetic linker exchange under reversible conditions has a great potential for generating *de novo* previously inaccessible COFs.^[59] Moreover, thanks to the rich chemistry of the C=N

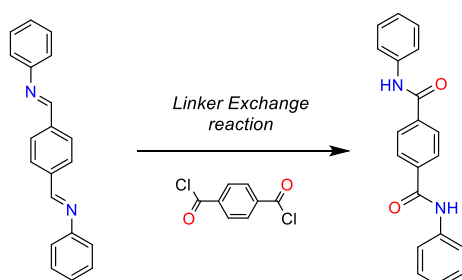
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linkage, the substitution of the linker can become irreversible (Scheme 5).

a) **Benzoxazole and benzothiazole linkages**



b) **Amide linkage**



Scheme 5. Different types of irreversible post-synthetic linker exchange reactions used to lock the imine-bond in COFs by PSMs.

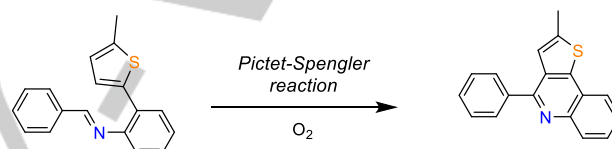
In 2018, Yaghi and co-workers reported a method to obtain benzoxazole and benzothiazole-linked COFs by exchange of the PDA component of ILCOF-1 with the geometrically equivalent moieties bearing the hydroxyl or thiol groups at the *ortho* position (Scheme 5a). The reaction, driven by the higher nucleophilicity of the amine group induced by the presence of the electron-donating moieties, led to the quantitative transformation in the isostructural COF-921 and LZU-192.^[60] After the substitution, the locking transformation to benzoxazole or benzothiazole took place through oxidative cyclization. As for the OPR version of the reaction, the control over the last stage was found to be critical to obtain a crystalline and chemically well-defined structure while avoiding undesired processes of interlayer transfer hydrogenation. For this reason, the optimization of the reaction condition led to the use of a water/DMF mixture under an atmosphere of oxygen at 85 °C. The higher crystallographic densities of the modified materials resulted in the substantial decrease of the BET surface areas (1550 for the benzothiazole and 1770 m² g⁻¹ for the benzoxazole) with respect to the parent material ILCOF-1 (2050 m² g⁻¹). The chemical stability of the benzoazole linkages was tested by immersion of the materials in acid (12.1 M HCl, 18 M H₂SO₄, 14.8 M H₃PO₄, and 9 M H₂SO₄ in DMSO) and basic (10 M NaOH) solutions for one day. In contrast with the imine COF precursor, the benzoazole materials exhibited remarkable chemical stability in all conditions.

The linker exchange method has also been demonstrated to be a viable post-synthetic strategy for the construction of highly stable amide-linked COFs (Scheme 5b).^[61] The pristine imine COF TzBA exchanged its 4,4'-biphenyldicarboxaldehyde (BA) component when exposed to the shorter but geometrically equivalent terephthaloyl chloride (TaCl). The reaction was carried out at low temperature for 48 h in dioxane/mesitylene, generating the

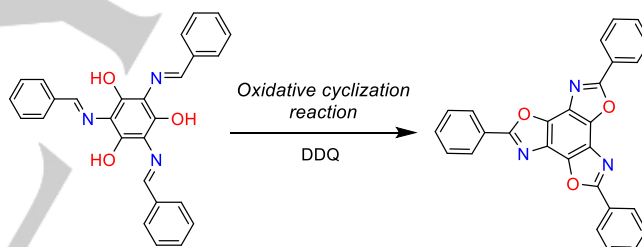
crystalline JNU-1. The driving force for the exchange reaction is in this case the higher electrophilicity of TaCl respect to dialdehyde BA that the authors determine by computing the HOMO – LUMO energies. The material was proved resistant to harsh acid conditions (10 M HCl) and mild basic environments (1 M NaOH) as well as temperatures up to 400 °C. When tested for Au(III) recovery from water solutions, the material showed high selectivity and the excellent adsorption capacity of 1124 mg g⁻¹, being larger than most of previously reported materials.

In a PSM approach, similar to the self-locking OPR, the building-blocks can be chosen to bear a reactive moiety in the *ortho* position, which can be employed for a consecutive irreversible reaction, typically being an oxidative cyclization. In contrast with the OPR method, if the energetic barrier for the oxidation is high enough, it is possible to isolate and characterize the imine-linked intermediate COFs. Only upon subsequent addition of an external oxidating agent the irreversible transformation of the linkage is completed. Two examples of this strategy were reported recently (Scheme 6).

a) **Thienopyridine linkage**



b) **Benzoxazole linkage**



Scheme 6. Different types of *ortho*-groups induced irreversible reactions used to lock the imine-bond in COFs by PSMs.

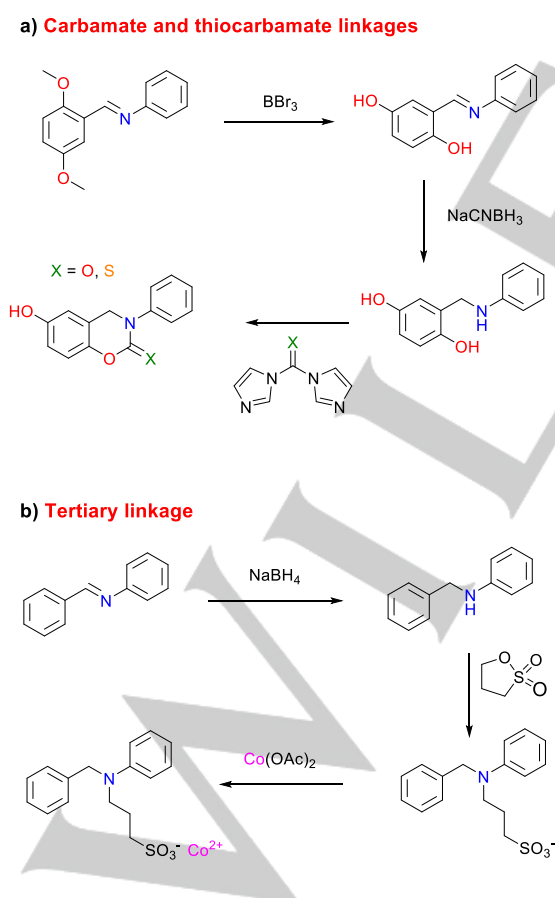
Recently, 2D COFs linked by the thieno[3,2-*c*]pyridine moiety were prepared via the Pictet–Spengler reaction (Scheme 6a).^[62] Initially, the Schiff base condensation between an aldehyde knot and an amine linker bearing a thiophene group at the *ortho* position generates the crystalline imine linked framework, that can be isolated and characterized. The reaction was carried out in a mixture of 1,2-dichlorobenzene/*n*-butanol/acetic acid in standard solvothermal conditions. The locking reaction is an oxidative cyclization process between the β-carbon of the thiophene and the C=N carbon and was performed using oxygen as molecular oxidant in a mixture of TFA and toluene heated at 100 °C for 2 days. While preserving the crystallinity and surface area of the pristine framework, the introduction of the new linkage was demonstrated to provide higher robustness to chemical agents (12 M HCl and 12 M NaOH at 50 °C for 1 day), thermic stress (up to 460 °C) and to the electron beam, which allowed fine imaging of the crystallites. Moreover, thanks to the extended π-conjugation and to the suitable LUMO and HOMO levels, the thienopyridine-linked frameworks were successfully applied for photocatalytic nicotinamide adenine dinucleotide (NADH) regeneration.

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Finally, Baek and co-workers demonstrated that by selecting the proper reaction conditions and specific monomers the imine formation can be completely decoupled from the oxidative cyclization locking (Scheme 6b).^[63] The tritopic knot 1,3,5-triamino-2,4,6-benzenetriol (TABT) was reacted with terephthalaldehyde (TPA) in standard solvothermal conditions in methanol and mesitylene. The imine-linked I-COF could be isolated and characterized but exhibited very poor stability in ambient moisture. The oxidative cyclization to the benzoxazole-linked BO-COF was then obtained at room temperature in dichloromethane (DCM) using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as molecular oxidant. The final material retained its topology and showed only a minor decrease in the BET surface area from 1906 m² g⁻¹ for the I-COF to 1687 m² g⁻¹ for the BO-COF. This loss was attributed to the slight reduction in pore size (from 1.70 to 1.65 nm) and crystallinity after oxidative cyclization. In turn, BO-COF displayed excellent thermal and chemical stability compared to the parent imine structure.

3.2. Multi-Step PSMs

As solution organic chemistry is not limited to single-step reactions, modification of reactive sites inside the pores of a COF can be extended to a sequence of solid-state reactions that can create high complexity functionalities while maintaining the overall connectivity of the framework. Two works have already been reported which exploits this strategy, thereby demonstrating the feasibility of a multi-step PSM on COF linkages (Scheme 7).



Scheme 7. Different types of irreversible multi-step reactions used to transform the imine-bond in COFs by PSMs.

Yaghi *et al.* described the first example of a multi-step PSM on imine-linked COFs, in which the imine-linked COF-170 was efficiently transformed into thiocarbamate-linked COFs (Scheme 7a).^[64] COF-170 synthesized solvothermally *via* condensation between (E)-3,3',5,5'-tetrakis(4-aminophenyl)stilbene (TAPS) and DMTPA served as the starting material for the synthesis of isostructural cyclic carbamate and thiocarbamate-linked COFs. This synthesis started first with demethylation of 1's methoxy groups, followed by reduction of the imine linkage with sodium cyanoborohydride and acetic acid in THF. This amine-linked COF was then treated with 1,1'-carbonyldiimidazole (CDI) or 1,1'-thiocarbonyldiimidazole (TCDI) and N,N-dimethylaminopyridine (DMAP) in DCM to yield cyclic carbamate and thiocarbamate-linked COFs, respectively. Noteworthy, these new linkages were never achieved with OPR equivalent reactions as they require multistep synthesis.

A multi-step PSM strategy was applied for the integration of catalytic active sites into the 1D open channels walls of a COF structure (Scheme 7b).^[65] The layered imine-linked TFPPy-PyTTA-COF was firstly treated with NaBH₄ to achieve the amine derivative. The reduced material was then reacted with 1,3-propane sultone generating by aminolysis a sulfonic acid functionalized COF linked by a tertiary amine moiety. In the last step the Co(II) salt of the acid was obtained by metathetical reaction with cobalt acetate. While the first and the last steps could be carried out at room temperature, the aminolysis of 1,3-propane sultone required 2 h reaction in refluxing toluene. The analysis on the purified Co²⁺@TFPPy-PyTTA material confirmed that 51% of the imine linkages were successfully modified. The resulting ionic COF was applied as catalyst in the cycloaddition reaction of CO₂ to epoxides demonstrating decent recyclability and outstanding catalytic activity.

4. Summary and Outlooks

The works highlighted in this Minireview illustrate how OPR and PSM strategies can be adapted from classical chemical synthesis and employed for the chemical modification and locking of the imine linkage in COFs. Currently, the large portfolio of COF structures available derive from a handful of covalent linking reactions that exhibit a reversible nature under reasonably mild conditions, among which the imine is the most widespread. However, the development of COFs with new topologies and higher structural complexity relies on the synthesis of novel monomers, which is inherently limited by the need for advanced organic synthesis. The exploration of new linkages and new reaction paths for the crystallization of COFs is the key for the development of novel functional porous materials. In this context the chemical transformation of imine COFs has revolutionized the field during the past five years and has become an essential tool for the synthesis of robust materials that can feature an extended π -conjugation and/or incorporate new pore functionalities. Although this research topic is still in its infancy, several functional materials have been designed through OPRs or PSMs and explored for photo/electro catalysis,^[38, 47, 66] electronics,^[41, 44] molecular separation,^[56] ionic capture,^[61] proton conduction,^[16b, 67] etc. (Table 1).

While offering practical pathways for the construction new COF-linkages, self-locking OPR methods often entail a non-optimal crystallinity of the material due to the reduced thermodynamic

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control that can be exerted on the reversible imine bond formation. On the other hand, this strategy has opened new routes for construction of COFs otherwise not accessible via PSM, such as the β -ketoenamine and phenazine-linked COFs. Noteworthy, it has been recently shown that the multi-component OPR and single-step PSM are potentially interchangeable strategies that can be used to tackle benzothiazole, quinoline and α -aminonitrile-linked COFs.^[47, 51] To date, however, the PSM product was always found being slightly worse in terms of yield and crystallinity, probably due to the difficulties deriving from the reactions at the solid state. Finally, despite being time demanding, multi-step PSM reactions prepared the ground for the construction of complex moieties at the linkage position of COFs.

With both methods a minimal loss in crystallinity in the product compared to the starting imine-linked COFs is inevitable. Due to the interference of the locking reaction in an OPR, the imine formation process is characterized by reduced reversibility. In PSM reactions the perturbation of the internal order derives from the harsh reaction conditions often used to modify the linkage. The surface area decreases as consequence of the lower crystallinity as well as due to the increased crystallographic density of the final materials. Clearly, while the crystallinity issue can be tackled by finely tuning the reaction conditions in OPR or using mild PSM reactions, the increase in crystallographic density is defined by the composition of the final linkage.

The field of the chemical modification of imine COFs will continue its growth during the next decade and the focus will likely shift from the robustness of the material towards the functionality and the conjugation of the linkages, which so far has not been sufficiently mastered. The potential increase in π -delocalization

and the electron acceptor/donor character that can be achieved by the transformation of the imine linkage to quinoline, phenazine and benzazole moieties hold a significant potential for applications in electronics, sensing and energy storage.^[44, 57a, 68]

We believe that joint theoretical and experimental efforts are required in order to cast light onto the in-plane charge transport through imine-linked 2D COFs and their derivatives. Moreover, the aforementioned cyclization reactions have the advantage of considerably increasing the rigidity of the linkage, element that could be well exploited to boost the solid-state photoluminescent properties of 2D and 3D COFs, currently limited by the rotational and vibrational relaxation pathways of the imine linkage resulting in non-radiative decay of the excited states.^[14, 69] In order to guarantee an efficient integration in real devices it will be required to adapt these synthetic strategies to the preparation of highly oriented thin films materials similarly to what it has been already done for the more classical boronate ester and imine-linked COFs, but also for β -ketoenamine and phenazine-linked COFs.^[70]

All in all, significant progress has been made toward the precise chemical manipulation of the imine linkage in COFs, which is undoubtedly the most tuneable bond among all currently employed reversible COF linkages. Interestingly, the knowledge gathered on the imine linkage locking approaches over the past decade is now being used towards formation of new pyrimidazole,^[71] benzofuran, and dioxin-linked COFs,^[72] highlighting the significance of the linkage locking approach beyond imines. We believe that further synthetic routes will be explored in the near future. Furthermore, the arsenal of modifications already available holds a great potential for the development of highly tailored crystalline and porous materials.

Table 1 Examples of OPR and PSM COFs discussed in the text and their proposed application.

COFs	Linkage	Form	Strategy	Thermal stability	Chemical stability	Application
FS-COM-1 ^[32]	β -ketoenamine	Self-standing membrane	OPR	300 °C	0 < pH < 7	Separation – ion/molecule sieving
LZU-192 ^[48]	Benzoxazole	Bulk	OPR	400 °C	9 M HCl 9 M NaOH Pure TFA	Photocatalysis – aerobic oxidation
TZ-COF-4 ^[47]	Benzothiazole	Bulk	OPR	450 °C	12.5 M HCl 12 M KOH 1 M NaBH ₄	Photocatalysis – H ₂ evolution
COF-DC-8 ^[42]	Phenazine	Bulk	OPR	510 °C	12 M HCl 14 M KOH	Electronics – NH ₃ , H ₂ S, NO, NO ₂ sensing
aza-COF-1 ^[16b]	Phenazine	Bulk	OPR	250 °C	12 M HCl 14 M KOH	Proton conduction
COF-300-AR ^[53]	Secondary amine	Bulk	PSM	500 °C	6 M HCl 6 M NaOH	Electrocatalysis – CO ₂ reduction
CCOF 6 ^[56]	Amide	Bulk	PSM	350 °C	12 M HCl 1 M NaOH	Separation – chiral HPLC
JNU-1 ^[61]	Amide	Bulk	PSM	400 °C	12 M HCl 1 M NaOH	Separation – Au ³⁺ capture

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The combination of functional building-blocks with customized linkages will lead to new COFs holding by design unprecedented properties for advanced applications.

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Keywords: covalent organic frameworks • imines • dynamic covalent chemistry • post-synthetic modification

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