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Fascinating isomeric covalent organic frameworks

Xitong Ren, Xinyuan Wang, Wen Song, Feng Bai and Yusen Li *

Isomeric covalent organic frameworks possessing the same chemical constitutions but different atomic arrangement structures and physicochemical properties are fascinating branches of covalent organic frameworks (COFs). However, the rational design and targeted synthesis of isomeric COFs remain conundrums, so the investigation of isomeric COFs is still in a fledging period. According to the diversity of frameworks, positional isomers with similar structures and framework isomers having distinct constructions are the main existing subspecies of isomeric COFs. In this review, we focus on the research progress and substantial achievements in this fascinating embranchment and systematically summarize and highlight the design principles of both positional isomeric and framework isomeric COFs, which will potentially facilitate further exploitation and investigation of novel isomeric COFs. The application and structure–property relationship of these isomeric COFs have been briefly introduced. Moreover, key constraints of current isomeric COFs and further advancement of this promising field are proposed and anticipated.

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Introduction

Isomerism is a fascinating phenomenon in chemistry, usually referring to molecules that share the same chemical formula but have different structures and properties. Isomerism greatly enriches the diversity and complexity of the chemical world, and it is very common in small molecules.[1] For instance, 2-chloropyridine and 3-chloropyridine are representative isomers that exhibit different boiling points, densities and many other physicochemical properties.[2] Notably, 2-chloropyridine is a very important intermediate in the fields of medicine and pesticide synthesis and the chemical industry, while 3-chloropyridine is usually produced as a by-product of the former isomer from thermal chlorination. Recently, isomerism has been developed in the fields of supramolecules and polymer frameworks such as molecular cages[3] and metal–organic frameworks (MOFs).[4] The concept of "framework isomers" was formally put forward by Zhou *et al.* in 2011,[4] and a series of isomeric MOFs with different network structures and properties but constructed from the same ligand and metal species were developed,[5,6] which endow MOFs with novel features and potential for application.

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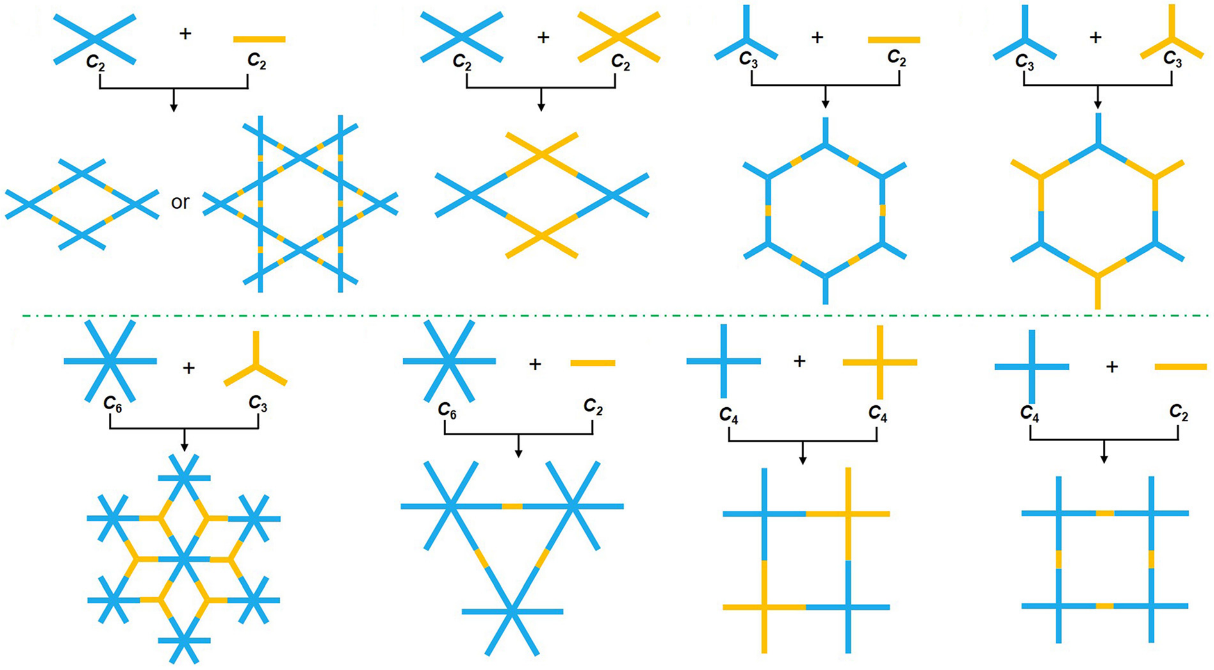

Fig. 1 Topology diagrams of 2D COFs constructed from different symmetric knots and linkers.

As emerging crystalline organic polymers, covalent organic frameworks (COFs) have drawn much attention and achieved rapid development since the seeding work of Yaghi in 2005.[7] Similar to MOFs, COFs possess long range ordered 2D or 3D periodic structures but are linked by various kinds of reversible covalent bonds such as imine, borate, olefin, amine, hydrazone and so forth.[8] Good stability and flexibility in design make COFs potential platforms for selective separation, optoelectronic devices, heterogeneous catalysis, biological therapy, chemical sensing, energy storage, *etc.*[8,9] However, the research on isomeric COFs is much confined compared with MOFs, which probably is ascribed to the robust covalent linkage, rigorous synthetic conditions and the limitation of monomer types.[10–12] It is difficult to control accurately the confined growth of covalent bonds, which is much less than the confined growth for all other linkages in polymer networks. A precursor with suitable symmetries is one of the key factors affecting the topology and isomerism of COFs. Specifically, for common two-component 2D COFs, only C_2 symmetric knots and C_2 symmetric linear linkers can afford a Kagome (**kgm**) or square (**sql**) topology,[12] while other symmetric building units such as $C_3 + C_2$, $C_3 + C_3$, $C_4 + C_2$, $C_4 + C_4$, $C_6 + C_2$, and $C_3 + C_6$ generally result in simplex topological frameworks (Fig. 1).[8,11] However, crystalline COFs are usually produced at high reac-

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tion temperature, with a long reaction time and in a specific solvent system which are helpful for reversible error correction of dynamic covalent bonds,[13] and as a result, stable thermodynamic frameworks with lower energy are commonly generated as the sole products even though the symmetries of building units are satisfied to construct isomeric frameworks in geometry.[14–16]

In recent years, great efforts have been devoted to exploring isomeric COFs, and the existence of both 2D and 3D COF isomers has been confirmed. Meanwhile, the targeted synthesis of isomeric COFs has been achieved by tactfully modulating molecular design or synthetic conditions. It has been demonstrated that slight differences in these isomeric COFs can contribute to marked differences in their electronic properties, optoelectronic performances, adsorption behaviours, *etc*., making isomeric COFs fascinating materials and showing their great significance in enriching the diversity and complexity of COFs. As a consequence, a review focusing on the advancement in the description of isomeric COFs is imminently needed to facilitate further development of COFs. To the best of our knowledge, there is no review that generalizes and summarizes the design principles, characteristics, and applications of isomeric COFs to date.

Classification of isomeric COFs

Overall, the finite isomeric COFs reported so far can be mainly divided into two categories: positional isomers and framework isomers. The positional isomeric COFs showcase similar frameworks, but the slight difference is that the position of some atoms or the relative orientation of chemical bonds (usually linkages) in the frameworks is different, and the slight difference in regions will contribute to extraordinary optoelectronic/electronic properties. In sharp contrast, the long-range ordered structures of framework isomers are significantly distinct, specifically in the degree of interpenetration for 3D COFs, stacking patterns and the diversity of topologies for 2D COFs. Therefore, the framework isomeric COFs typically exhibit distinct pore structures and result in selective adsorption behaviour.

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Positional isomers

According to the achievements of current research, the positional isomeric COFs can be obtained from three paths (Fig. 2): (i) exchanging the functional groups of building units for co-condensation, which is relatively easy to achieve and the discrepancy of these isomeric COFs generally embodies in linkages (*e.g.*, –C=N– and –N=C–); (ii) controlling the accuracy of the relative orientation of linkages, which can give rise to networks with the same topology but different geometries and pore channels, for example, rhombuses and parallelograms; and (iii) utilizing isomeric monomers as building blocks to perform the polymerization process, thereby affording isomeric frameworks, and suitable isomeric monomers are the crucial elements.

Indeed, COFs with the same topologic framework but different positional linkage structures are common, but investigations of the structure–property relationship originating from positional linkages are scarce.[17,18] In 2019, Seki *et al.* successfully constructed two positional isomeric frameworks (***C*-AntPy** and ***N*-AntPy**) from 1,3,6,8-tetrasubstituted pyrene and 9,10-disubstituted anthracene and investigated the property difference of these isomers (Fig. 3).[19] Not surprisingly, ***C*-AntPy** and ***N*-AntPy** present similar chemical constitutions as demonstrated by FT-IR and solid-state ^{13}C NMR spectroscopy. However, the position of the –C=N bond slightly affects the absorption and photoluminescence maxima of the two positional isomer films. Intriguingly, ***C*-AntPy** revealed a great extent of oxidation after I_2 doping, which was confirmed by the increased absorbance, EPR signal, photoconductivity and conductivity, but ***N*-AntPy** showed no significant changes before and after doping, which proved that the linkage position does play a crucial role in the optoelectronic performance of these covalently linked materials.

The directionality of linkages also has an impact on the stacking of COFs and gives rise to isomeric structures. In 2018,

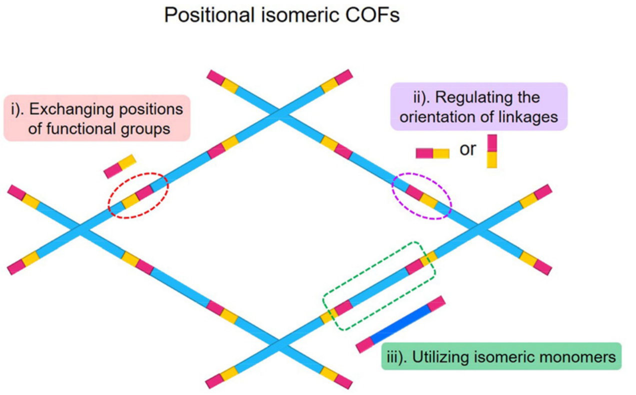

Fig. 2 Design principles for positional isomeric COFs.

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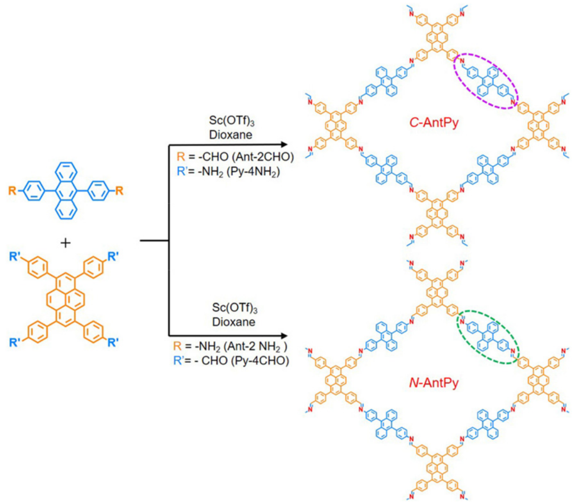

Fig. 3 Synthetic routes to positional isomeric ***C*-AntPy** and ***N*-AntPy**. Reproduced with permission from ref. 19. Copyright 2019, Royal Society of Chemistry.

Zamora *et al.* reported that **IMDEA-COF** systems were able to show two possible pore isomers due to the variable orientation of the imine bonds, that is, a big-pore isomer with flat COF layers and a small-pore structure with corrugated COF layers (Fig. 4a).[20] The calculated cohesive energy values for the possible structures of these isomers indicate that the big-pore isomer is energetically favoured when electron-donating building blocks are employed. In comparison with the experimental data, **IMDEA-COF-1** is concluded to be a mixture of big- and small-pore conformations in the AB stacking mode, whereas **IMDEA-COF-2** is predicted to be a unitary AA stacking big-pore structure due to the existence of electron-rich hydroxyl groups. In comparison to pure phase **IMDEA-COF-2**, the π–π interaction between pyrene units enables minimization thanks to the particular complex structure of **IMDEA-COF-1**, so the non-radiative energy dissipation is inhibited and a green colour emission at 501 nm with an absolute photoluminescence (PL) quantum yield of 3.5% is exhibited.

Utilizing enantiomeric monomers as building blocks or modifying COFs by chiral moieties is an effective route to chiral isomeric COFs.[21] The precise control of imine band orientation was first achieved in on-surface synthesis by Wang's group *via* the steric hindrance of chiral monomers.[21b] When prochiral PDA monomers with phenyl substituents are used to couple with 1,3,5-tris(4-aminophenyl)benzene (TAPB), the precursors are randomly distributed in the obtained distorted achiral hexagonal frameworks and the orientations of C═N linkages are variable. For comparison, the configuration of the imine bonds can be well controlled *via* prochiral DCPDA

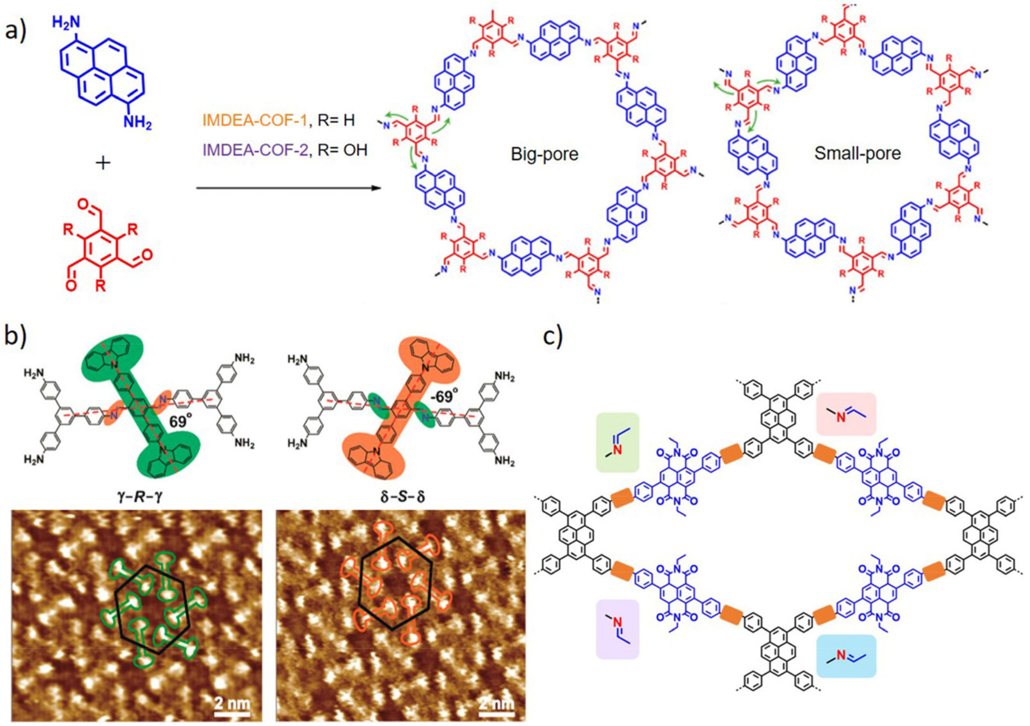

Fig. 4 (a) Schematic representation of the syntheses of IMDEA-COF systems by condensation of a tritopical aldehyde (1,3,5 benzenetricarbaldehyde, where R = H; or 1,3,5-triformilfloroglucionol, where R = OH) and 1,6-diaminopyrene (DAP), showing two possible pore isomers. Reproduced with permission from ref. 20. Copyright 2018, American Chemical Society. (b) Molecular models of the energetically favored TAPB-DCPDA-TAPB fragments and high-resolution STM images of CW-COF$_{\text{TAPB-DCPDA}}$ and CCW-COF$_{\text{TAPB-DCPDA}}$. Reproduced with permission from ref. 21*b*. Copyright 2020, American Chemical Society. (c) Schematic representation and the possible orientations of imine bonds in TAPPy-NDI COF. Reproduced with permission from ref. 22. Copyright 2021, Wiley-VCH.

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precursors with two bulky carbazole substituents, which is attributed to the large rotation angle of the substituent relative to the skeleton (Fig. 4b). Consequently, highly regular 2D homochiral CW-COF$_{\text{TAPB-DCPDA}}$ and CCW-COF$_{\text{TAPB-DCPDA}}$ were successfully prepared *via* an on-surface reaction on HOPG and could be distinctly observed *via* high-resolution scanning tunnelling microscopy (STM) images (Fig. 4b).

Since the accurate control of imine bond orientations has been achieved experimentally, Bredas and co-workers have systematically studied theoretically the effect of imine orientations in the TAPPy-NDI COF skeleton (Fig. 4c).[22] Considering three possible conformations of the imine bond in imine–NDI–imine segments and four types of connections between the imine bond and TAPPy, twelve isomeric structures would be generated for the TAPPy-NDI COF. Two *anti*- and two *syn*-conformations (A1, A2 and S1, S2) were selected as representative isomers to examine the impact of imine orientations on their crystal structures, electronic band structures, electronic coupling, and effective masses. According to the calculations, the A2 isomer has the most energetically stable structure, with the largest band gap and much smaller effective mass than those of the other isomeric conformations, suggesting that the imine orientations have a remarkable effect on the stacking pattern of COF layers and thus on the charge-transport properties of COFs.

Subsequently, the photophysical properties and photocatalytic performance of some positional isomeric COFs have been investigated. Thomas *et al.* elucidated the effect of imine linkage on photocatalysis *via* comparing the H_2 evolution performance of donor–acceptor DCNA COFs (D–C=N–A) and DNCA (D–N=C–A) COFs.[23] After protonation by ascorbic acid (AC), all DCNA_AC COFs exhibit enhanced photocatalytic H_2 evolution performance than the corresponding DNCA_AC COFs, which is ascribed to the broader absorption band and more efficient charge-transporting ability of DCNA_AC COFs. H_2 evolution can be achieved at 27.9 mmol h^{-1} g^{-1} for the DNCA-1_AC COF with the strongest nitrogen-triazine donor–acceptor combination. A similar tendency is also observed in isomeric oligo(phenylenevinylene)-based imine COFs[24] and benzothiadiazole-based imine COFs,[25] which further confirms that the positional isomerism of the linkages does possess significant influence on COF properties and performances.

Recently, positional isomers have been extended to olefin-linked COFs by employing suitable isomeric linkers. Two isomeric olefin-linked COFs (v-2D-COF-NO1 and v-2D-COF-NO2) were dexterously synthesized from *trans* and *cis* configurations of benzobisoxazole *via* benzobisoxazole-mediated aldol polycondensation (Fig. 5).[26] The two isomeric COFs possessed similar crystalline structures, morphology, stability, specific surface areas and pore sizes. Although their functional groups and elemental compositions are the same, the photophysical and electrochemical properties of these isomers are distinct. Specifically, v-2D-COF-NO1 with *trans*-benzobisoxazole exhibits a broader optical absorption capacity, narrower band gap, better photoelectrochemical performance and faster photocatalytic hydrogen evolution rate than v-2D-COF-NO2 with *cis*-benzobisoxazole, which presumably originate from the better in-plane conjugation and charge carrier migration of v-2D-COF-NO1 as revealed by DFT calculations.

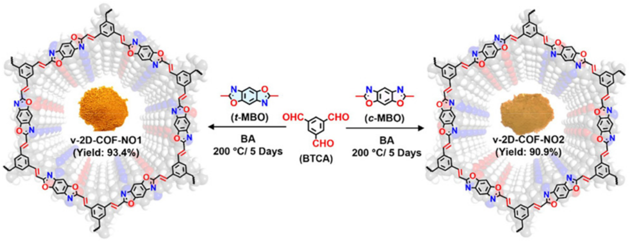

Fig. 5 Synthesis of isomeric v-2D-COF-NO1 and v-2D-COF-NO2 *via* the aldol-type polymerization between benzene-1,3,5-tricarbaldehyde (BTCA) and 2,6-dimethylbenzo[1,2-*b*:4,5-*b*′]bisoxazole (*t*-MBO) or 2,6-dimethylbenzo[1,2-*b*:5,4-*b*′]bisoxazole (c-MBO). Reproduced with permission from ref. 26. Copyright 2022, American Chemical Society.

Framework isomers

In contrast to the subtle discrimination of the positional isomeric COFs, the long-range ordered periodic structures of framework isomers are quite different, and hence their unit cell parameters, pore channels, and adsorption behaviours are profoundly different. The interpenetration isomerism of 3D COFs, stacking model transformation and topological isomerism of 2D COFs (Fig. 6) have been observed and most of them were established by regulating the synthetic procedure and synthetic conditions and combining promoted synthetic protocols. Among them, interpenetration isomerism is preferentially observed in 3D COFs and subject to the directional covalent connection between the rigid precursors; the stacking model transformation is relatively difficult to achieve for the eclipsed AA stacking mode, which is generally energetically stable; and the essential premise for topological isomerism of COFs is that the symmetries of building blocks match to form two or more topologies in geometry. Therefore, topological isomers are more devisable than the other two categories.

The representative 3D COF-300 is known as a 5-fold interpenetrated diamond structure (***dia-c5*** topology) and is syn-

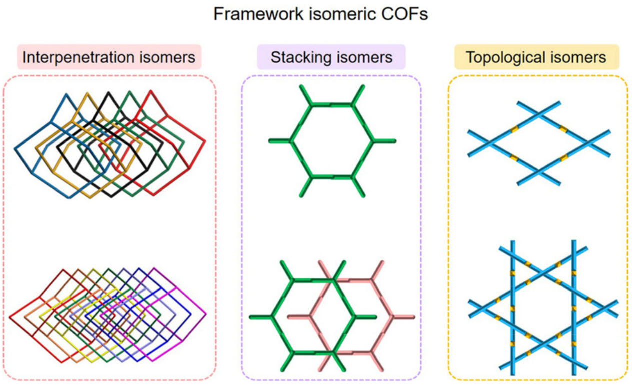

Fig. 6 Schematic diagram of framework isomeric 3D and 2D COFs.

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thesized *via* the conventional co-condensation solvothermal method at 120 °C for 3 days.[27] Interestingly, an aging process in which the precursor solution of COF-300 is stood at room temperature for 3 days and then maintained at 50 °C for 3 days before heating at 120 °C can be conducive to forming an interpenetration isomer with a 7-fold interpenetrated diamond topology (***dia-c7***, Fig. 7).[28] Despite the essentially identical constitution and similar stability, the two COF-300 isomers are structurally different, which was unambiguously identified by PXRD and powder rotation electron diffraction (RED) analyses. More importantly, it was demonstrated that the aging process maintained below 60 °C enabled sufficient time for the controlled synthesis of the thermodynamically stable ***dia-c7*** COF-300. However, this has been so far the only example of interpenetration isomerism, which probably arises from the fact that strongly oriented covalent linkages are unlikely to afford interpenetration diversity.

For 2D COFs, the eclipsed AA stacking mode is generally an energetically stable structure; therefore, the staggered AB stacking structure is extremely scarce. The Dai group proposed a tandem conversion strategy to successfully produce highly crystalline CTF-1 with AA and AB stacking orders.[29] The crystalline orange CTF-1 with the staggered AB stacking mode can be easily obtained under the catalysis of trifluoromethanesulfonic acid at 250 °C for 12 h, and the staggered structure is able to transform into greenish CTF-1 with an eclipsed AA stacking order through annealing at 350 °C under nitrogen. The acidity and loading amount of superacid exhibit tremendous influence on the quality of final AA stacked CTF-1 (Fig. 8). The driving force for transformation from the AB to AA stacking mode is that the AA stacking order is a more thermodynamically stable product and exhibits stronger interlayer interaction. The two isomeric CTF-1 frameworks exhibit the same chemical constitution but different light absorption capacities and distinct surface areas. The BET surface area of CTF-1-AA (646 m^2 g^{-1}) is much larger than that of CTF-1-AB (22 m^2 g^{-1}) which is probably caused by the staggered layer structure and the existence of CF_3SO_3H within the interlayers in CTF-1-AB. Moreover, the staggered CTF-1-AB has been demonstrated to show much better photochemical performance and saturated photocurrent density than isomeric CTF-1-AA in follow-up work.[30]

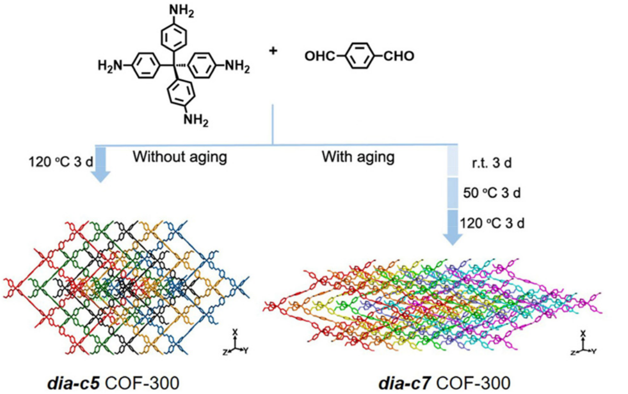

Fig. 7 Schematic presentation of two interpenetration isomers of COF-300. Reproduced with permission from ref. 28. Copyright 2018, American Chemical Society.

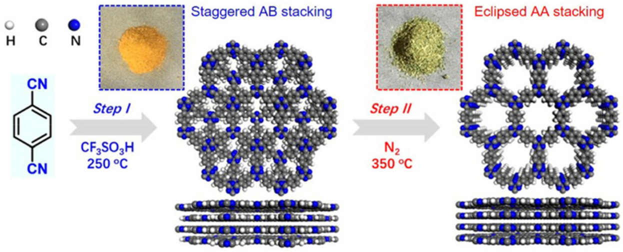

Fig. 8 Schematic diagram of the two-step synthetic pathway. Images in the blue and red dashed boxes are powders obtained in Step I and Step II, respectively. Reproduced with permission from ref. 29. Copyright 2020, American Chemical Society.

The framework isomerism of 2D COFs was first identified in on-surface synthesis of a single-layered COF in 2017, which was constructed from representative D_{2h} symmetric 1,3,6,8-tetrakis(*p*-formylphenyl)pyrene and C_2 symmetric ditopic linear diamine.[31] Rhombus, parallelogram, and Kagome networks were apparently observed on the graphite surface using a scanning tunneling microscope (STM, Fig. 9), while the conventional solvothermal method only afforded bulk quadrate networks.[32] The presence of water, the reaction temperature and the molar ratios of monomers can impact the equilibrium control and the formation of well-ordered networks. Besides, two types of quadrate networks with high packing densities are predominant products at relatively high concentrations, while the Kagome networks with low packing densities prefer to form under dilute conditions, which is similar to the concentration effect on orienting supramolecular assemblies.[33]

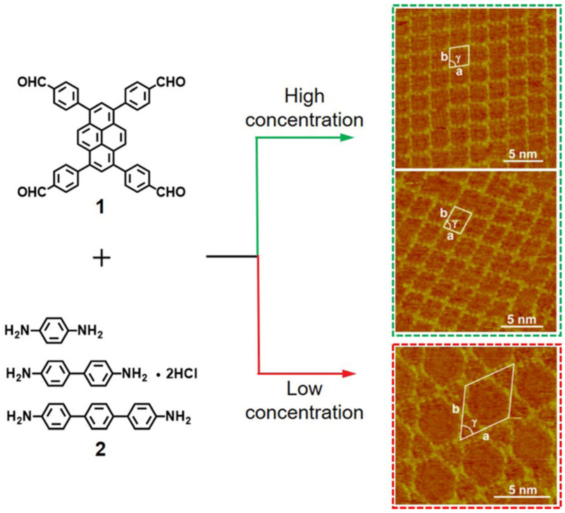

Fig. 9 Overview of the three morphological single-layered COFs formed by polymerization of 1 and 2. Reproduced with permission from ref. 31. Copyright 2017, American Chemical Society.

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Subsequently, the Zhao group achieved the controllable synthesis of 2D framework isomeric COFs *via* regulated reaction solvents in 2020.[34] Similarly, 4′,4‴,4‴″,4‴‴′-(ethene-1,1,2,2-tetrayl)tetrakis([1,1′-biphenyl]-4-carbaldehyde) (ETTBC) with D_{2h} symmetry and C_2 symmetric 2,5-diaminotoluene (DAT) were selected as the building units to prepare isomeric COFs. After screening the solvent systems, a single-pore framework with the AA stacking mode (SP-COF-ED) was synthesized in a mixture of mesitylene/dioxane, whereas a dual-pore isomer (DP-COF-ED) was constructed in the system of *n*-butyl alcohol/*o*-dichlorobenzene. Interestingly, the directional transformation process can only be performed from DP-COF-ED to SP-COF-ED, suggesting that the SP-COF-ED might be the more thermodynamically stable product. The significant difference in isomeric structures was definitely revealed by the distinct PXRD patterns and N_2 adsorption–desorption isotherms. In addition, DP-COF-ED displays better hydrolytic stability and more sensitive stimuli-responsiveness toward *n*-hexane vapor than the SP isomer, providing a good example to shed light on the structure–property relationship of isomeric COFs (Fig. 10a).

However, the rigorous synthetic system for conventional co-condensation COFs is one of the key issues which will hinder further investigation of the fascinating isomerism of COFs. The crystallinity of the COFs is affected when the synthetic solvent is varied.[35] To solve this conundrum, a "two-in-one" synthetic strategy was proposed and utilized to synthesize COFs in various kinds of solvents by Chen *et al.*,[36] which provides a new possibility for exploring the isomerism of COFs. Primarily, three A_2B_2 isomeric monomers (*p*-TetPB, *m*-TetPB, and *o*-TetPB) were elaborately designed and synthesized to prepare five kinds of isomeric COFs.[37] Among the three monomers, *p*-TetPB and *m*-TetPB are able to assemble into hexagonal **kgm** nets in aprotic solvents such as THF, and into monoclinic **sql** frameworks in protic alcohols. However, *o*-TetPB can only afford the square architecture in either protic or aprotic solvents due to the own configuration mismatch. These iso-

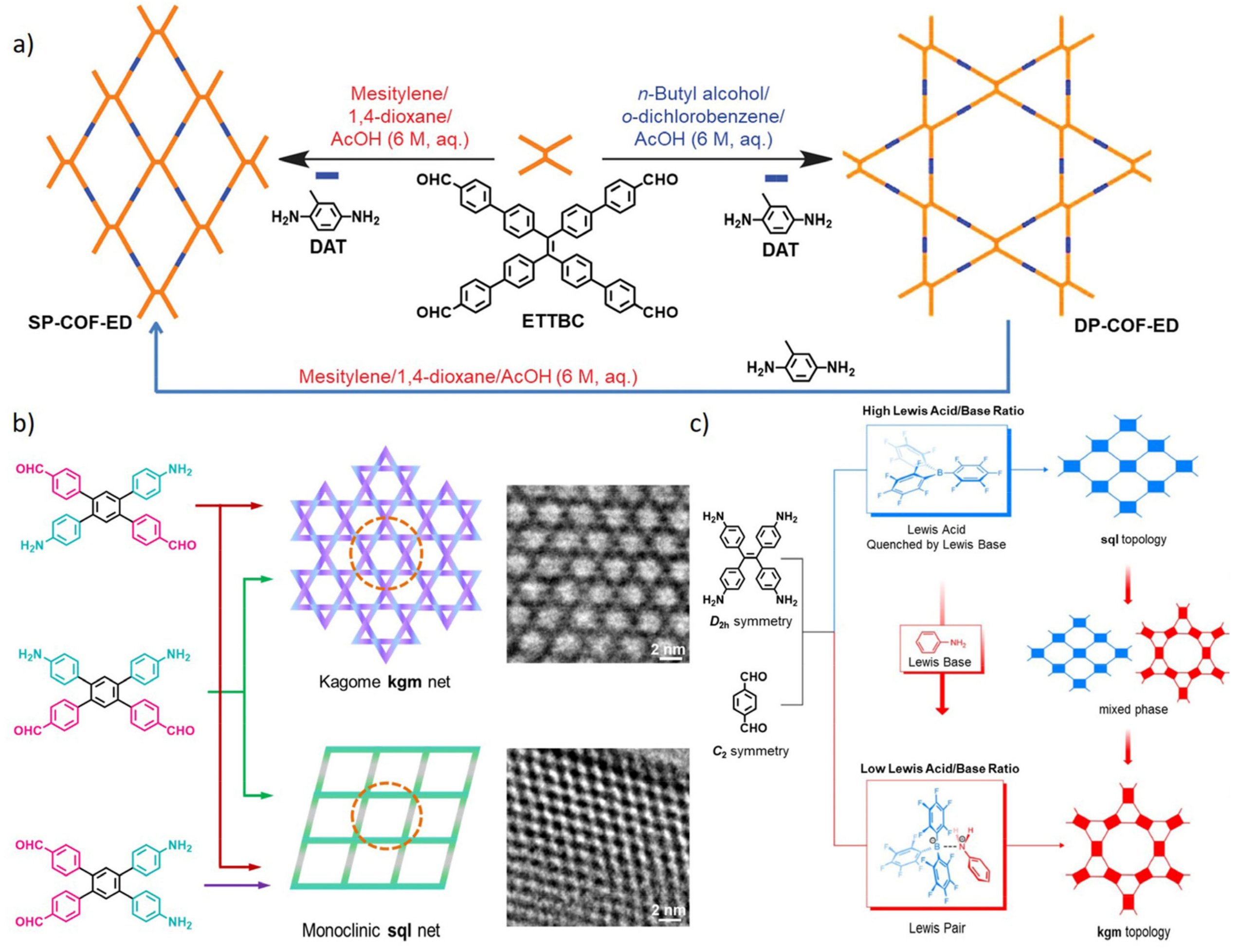

Fig. 10 (a) Controllable synthesis of SP-COF-ED and DP-COF-ED isomers and the transformation from one isomer to the other. Reproduced with permission from ref. 34. Copyright 2020, Chinese Chemical Society. (b) The illustration of isomeric COFs from isomeric bifunctional monomers. Reproduced with permission from ref. 37. Copyright 2021, Wiley-VCH. (c) Tuning of topology by adjusting the ratio of bulky organoboron as a Lewis acid and aniline as a Lewis base. Reproduced with permission from ref. 40. Copyright 2022, Springer Nature.

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meric COFs also showcase the same constitutions but different crystalline structures and N_2 adsorption capacities. Furthermore, the prominent distinction in the regular structures can be confirmed by the clear hexagonal honeycomb structure and uniform rhombic pores visualized in their corresponding HRTEM images (Fig. 10b). The difference in pore characteristic enables these isomeric COFs to selectively adsorb vitamin B_{12} guest molecules. Also, two biphenyl-based bifunctional monomers with or without protective groups for aldehydes have been indicated to be capable of fabricating isomeric COFs with the **kgm** and **sql** topologies *via* readily regulating the synthetic solvents and the concentration of precursors.[38] The mentioned concept of "from isomeric monomers to isomeric frameworks" has been extended to the synthesis of isomeric COFs with triangular pores.[39] The above examples demonstrate that the "two-in-one" strategy might be a proven and effective method for the construction of 2D constitutional isomeric COFs.

Apart from synthetic solvents, catalysts would be another crucial element for the formation of periodically ordered structures of COFs. Very recently, tris(pentafluorophenyl)borane (TPFB) was applied as a Lewis acid catalyst to realize the topological structure tunability of 4PE-1P-COF[40] which has been known as the typical **kgm** topology COF since 2014.[14] The size of TPFB is larger than the triangular pores in the **kgm** topology but smaller than the quadrangular pores in the **sql** framework, so COF-820 with the **sql** topology was isolated through the steric effect of bulky organoboron. The topology can be well modulated from pure phase **sql** COF-820 to the mixed phase and then to pure phase **kgm** 4PE-1P-COF by adding an additional amount of aniline to quench the acidic sites in TPFB (Fig. 10c), offering a new option for targeted synthesis of isomeric COFs.

Summary and perspective

The design principle based on the position of linkages and the symmetry matching of precursors has established the basis for synthesizing isomeric COFs. The distinct arrangement of atoms and molecules induced framework isomerism, which not only enriches the diversity, but also has significant implications for expanding the potential applications of COFs. Although some preliminary developments have been achieved, there are still many fundamental issues to be addressed in many aspects.

First of all, positional isomeric COFs, particularly the common species that exhibit different positional linkages (*e.g.*, C=N and N=C) but the same topological structures, have not received enough attention, even though some results have indicated that the slight differences in structures can generate remarkable photophysical properties.[23–26] Amplification of the structural and feature differences in a rational way may be one of the key factors in promoting further development of positional isomers. A possible and effective protocol could be to incorporate guest molecules to introduce discriminative interactions between guests and isomeric frameworks, so these isomers can present markedly different properties. The phenomenon of "big distinction originated from little difference" would attract more interest and encourage further exploration of positional isomeric COFs. Meanwhile, the orientation of linkages has been demonstrated to be a significant factor in layer stacking,[41] but achieving accurate control of the spatial direction of linkages remains a challenging goal. Intensive studies of the growth mechanism of COFs and exploration of key factors affecting the orientations of covalent bonds will be of practical guiding importance for this target.

Second, the episodic nature of topologic isomers severely impedes the development of isomeric COFs. Although the geometry of precursors is theoretically satisfied to form isomeric frameworks, the restricted synthesis conditions of co-polymerization COFs constrain the isolation of isomers. It has been indicated that the solvent system, precursor concentration, temperature and catalyst all affect the isomerism, and therefore precise regulation of synthetic conditions is a reasonable path to accelerate the targeted preparation of isomeric COFs. However, it is difficult to realize in practice due to the complicated effects of those issues on the polymerization rate, nucleation, and crystallization. There is also an urgent need to pullulate novel synthetic strategies for selectively and readily producing the desired kinetically or thermodynamically favoured isomers. Besides, the utilization of specific structures and the investigation of structure–property relationships for framework isomeric COFs are far from being sufficient. Currently, the utilization of framework isomeric COFs mainly depends on the distinct pore sizes, such as selective adsorption[34,37] and delayed drug release.[38] The underlying electronic, magnetic and optoelectronic properties of framework isomers are worth in-depth investigation due to the remarkable differences in the arrangement, stacking mode and interlayer interaction.

Last but not least, the expansion of isomeric building units is one of the pivotal elements in prolonging the species and scope of isomeric COFs. It has been demonstrated to be the effective path to construct isomeric chiral COFs,[21] high-valency polycubane COFs[42a] and unprecedented topological 3D COFs[42b] *via* utilizing suitable isomeric monomers or steric control modified molecules as building blocks. Therefore, isomeric monomers with different characteristics and diversiform symmetries are favourable for constructing novel isomeric COFs. For instance, C_{2v} symmetric monomers with one elongated branch can theoretically produce 2D COFs with two different kinds of hexagonal honeycomb pores when combined with C_2 symmetric linear linkers,[43a] and COFs possessing uniform irregular hexagonal pores or a dual-pore structure composed of regular and irregular hexagonal pores are afforded when co-polymerized with D_{3h} symmetric linkers;[43b] K-shaped metallosalphen-based "two-in-one" monomers are able to form three kinds of networks with triangular, quadrangular and octagonal pores, triangular and irregular hexagonal pores, triangular pores with different sizes and irregular hexagonal pores, respectively.[43c] Moreover, it is possible to construct

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topological isomeric COFs from positional isomeric monomers *via* rational design, such as the representative 9,9′-spirobi[fluorene]-3,3′,6,6′-tetracarbaldehyde and 9,9′-spirobi[fluorene]-2,2′,7,7′-tetracarbaldehyde.[44] Exploitation of these novel building units provides a foundation for the preparation of novel isomeric COFs.

In summary, isomeric COFs have been initially studied in the last five years, and the construction of isomeric COFs has been realized from accidental to directed synthesis. The unique features and applications of isomeric COFs have also been explored. These fascinating achievements will attract more attention towards the intriguing and meaningful isomerism in COF fields and accelerate the development of isomeric COFs. We believe that with the development of novel precursors and further investigation of structure–property relationships, isomeric COFs will be more abundant and can function as possible platforms for many applications.

Conflicts of interest

There are no conflicts to declare.

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