



Review: Recent Advances in Synthesis and Characterization of Covalent Organic Frameworks (COFs)

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Abstract

Covalent organic frameworks (COFs) are a type of porous material that exhibits an emergent crystalline group. Through covalent bonds, it assembles organic fundamental components in an orderly framework with atomic clarity. To form strong bonds, COFs are primarily composed of light elements such as H, B, C, N, O, and Si. Examples include well-known and functional materials such as diamond, graphite, and boron nitride. The variety of defined features in COFs has exploded in recent years. This review critically highlights recent advancements in COF design principles. Porosity, structural regularity, and functionality are all incorporated into the design. Additionally, the review discusses synthetic procedures, the characterization of COFs products as well as challenges associated with COFs materials, are discussed.

Keywords: *Covalent Organic Frameworks, Synthesis, Building units, Solvothermal and Crystalline.*

Introduction

The chemistry of using covalent bonds to link organic molecules together to form discrete zerodimensional (0D) molecules and

one-dimensional (1D) chains (polymers) had been extensively studied, but covalent chemistry was seldomly investigated in making

structures that extended in two and three dimensions (2D and 3D, respectively) (Figure 1).[1]. Thermodynamic robustness of covalent bonds, such as those seen in diamonds and boron carbides, were combined with the flexibility of organic subunits in COF architectures made up of light elements (B, C, N, O, and Si). Prolonged critical and creative challenges had hindered progress in the field [2–5]. To commence, the poor solubility of 2D and 3D frameworks inhibits future creation and difficult isolation of crystalline compounds, with the exception of 0D and 1D complexes. Second, the number of components that may be made by linking certain architectural geometry to 2D or 3D extended structures is virtually unlimited, making their development more difficult. The first difficulty was overcome by a group of researchers which disclosed that using reversible condensation procedures to crystallize 2D COFs in which the molecular basic components are entirely coupled via strong covalent bonds [2]. The second hurdle was addressed by illustrating how reticular chemistry design ideas may be applied [6]. In order to achieve thermodynamic flexibility in reversible covalent-bond production events, the synthesis of both 2D and 3D COFs is subject to two fundamental problems: (i) the essential element assembly; and (ii) the synthetic method, which contains reaction media and circumstances (temperature, ratio, time, and volume of the reaction media). These compounds can self-assemble into the thermodynamic minimal configuration given the nature of the reversible bond. When a material is amorphous or contains imperfections that are thermodynamically less favourable than a regulated framework, twirling bonds and nonequilibrium topologies arise. This released energy is what propels the framework's development and crystallization [1]. Conversely, while reversibility does not prohibit systemic order, it is vital to avoid the production of amorphous frameworks since the bulk of molecular fundamental elements cannot endure the intense heat required to build crystalline structures. Chemically inspired dynamic covalent chemistry (DCC) was used to synthesize thermally resilient expanded crystalline COFs, resolving the issue in part [7,8].

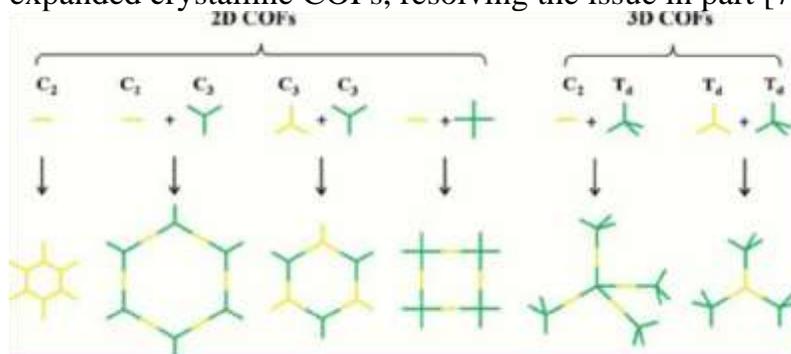


Figure 1: The arrangement of basic components to develop COFs with distinct geometries. [9].

Covalent bond formation of building units

The arrangement of the basic components must meet two conditions in order to generate a crystalline COF: (i) the COF assembly process must be reversible, and (ii) the geometries of the basic components must be well conserved in the COF. In aspects of (i) the fundamental elements should have structural features that favour dynamic covalent bond formation, (i.e., no irreversible side reactions), and the reaction system should be totally made up of interchangeable monomers, oligomers, and polymers. Concurring to the second criteria, the basic units must be conformationally steady, and the positioning of the bonding molecules must be definite [10]. Various reversible paths have been explored in an effort to tie the first measures for operational COF synthesis as shown in (Figure 2, a - g)[7,11–15].

Some organic linkages were acknowledged as being occupied in the development of COFs, including B-O (boroxine, boronate ester, spiroborate, and borosilicate), C=N (imine, hydrazone, and squaraine), and C=N (-ketoenamine, imide, and amide) [9].

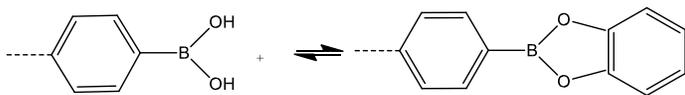
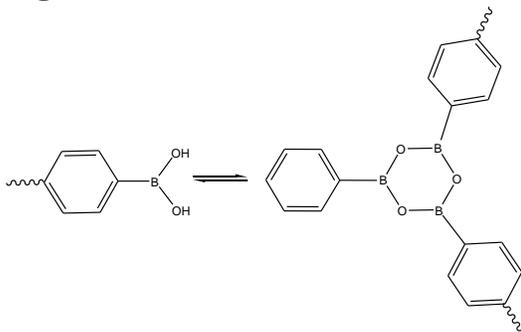
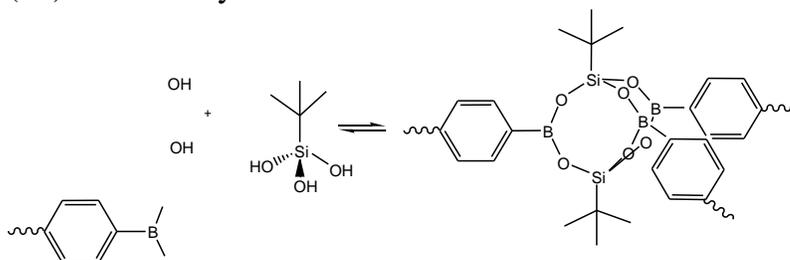


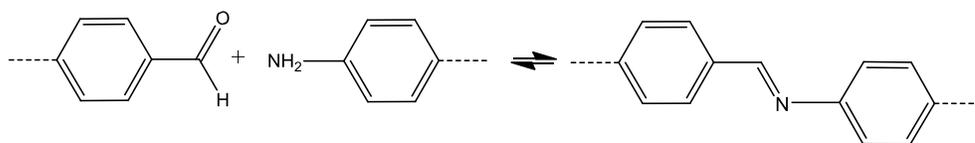
Fig.2a. Boronate ester formation



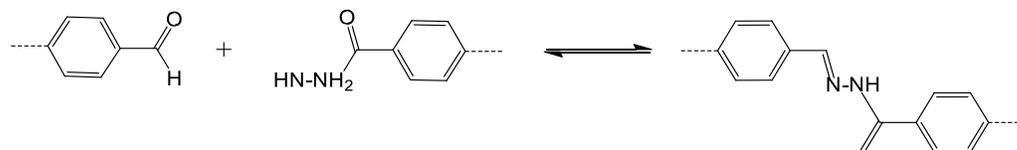
(2b) Boron anhydride formation



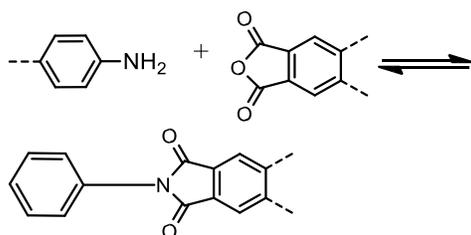
(2c) Boron anhydride formation



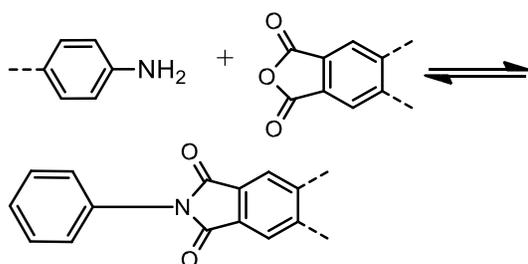
(2d) Imine formation; Note: the reactions d and e are based on the imine bonds(C=N) by which various COFs have been processed



(2e) Hydrazone formation



(2f) Imide formation



(2g) β -ketonamine,amide formation (C-N,)

Design and principles

COF materials can be synthesized employing reticular chemistry concepts, comparable to metal-organic frameworks (MOFs) [3,16]. The structures and pores of COFs can be built using a topology model (Figure 2, above) based on geometric matching of assembly pieces. Polygons are often made up of loops and binder subunits, with topologies controlling the geometry of the polygon and parameters determining the porous structure.

The design methodologies utilized to make other covalently-bonded porous solids were applied for the synthesis of COFs. A range of porous conjugated polymers were successfully produced via coupling processes with inflexible subunits [17,18]. Recently, rigid key components were utilized to build expanded microstructures, and this method was used to synthesis the bulk of porous COFs compounds. The pore size of COFs is thus determined by the molecular size of the building components, whilst the topology of the porous structure is determined by the shape of the building units. Obviously, in the COF process, porosity factors do not guarantee crystalline development. Strong covalent bonds, on the other hand, generally result in disordered architectures, as mostly seen commonly in porous organic polymers[19,20]. As a consequence, unlike amorphous organic polymers, establishing design regularity is the most significant challenge in the intended manufacture of COFs. The identification of relevant processes that enable thermodynamic equilibrium regulation throughout bond formation, permitting for self-correction and the development of thermodynamically stable crystalline structures, is a significant problem in the synthesis of COFs. The development of dynamic covalent bonds should be induced by reactive groups in the basic components. The construction blocks should also be visually robust, with a clear bond formation orientation[21]. The synthesis of characteristic pore architectures requires the rational design of rigid building components and the precise selecting of synthetic processes [22]. The reversible creation of covalent bonds is anticipated to be crucial in the fabrication of crystalline COFs, much as it is in zeolite synthesis [23]. Even if these requirements are met, the construction of architecturally consistent COFs remains an open question.

Synthesis reactions and Methods

The difficulty of synthesizing COFs with high porosity and crystallinity could still be addressed. For improving coordination involving framework development and crystalline, the right temperature and pressure are necessary, as well as the right solvent mixtures and ratios. Integrating building units in a particular solvent in a vessel, degassing, capping, and warming at a required temperature for a fixed amount of time all are part of this technique.[10]. To fully determined powdered COFs, the product is retrieved, cleansed, and treated. The inclusion of mesitylene-dioxane as a liquid solution aid in the regulation of monomer dispersion in solutions, speeding up COF formation. A

regulated system also provided that enough water was supplied for proper COF crystal formation [7]. COFs are made at high temperatures (80–120 °C) and low reaction pressures [9]. Applying a few drops of an acid (aqueous acetic acid) as a catalyst also resulted in crystalline COFs products [13,24].

Various investigators have focused on enhancing the synthetic capability in a number of methods following scientists synthesized the first COF (COF-1), (Figure 3), using the solvothermal technique. COFs are synthesized via solvothermal, Ionothermal, and microwave synthesis methods.

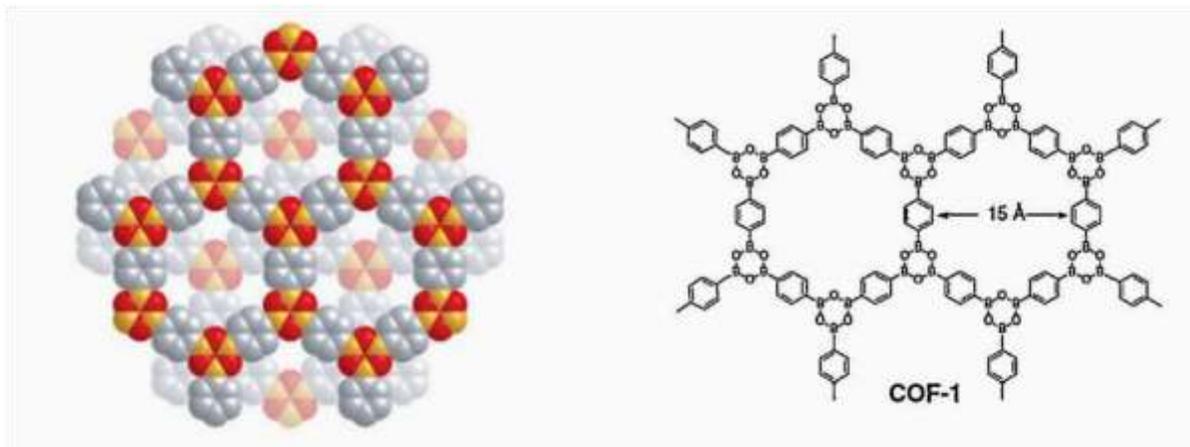


Figure 3: Images of COF-1 along c axes. Carbon, boron, and oxygen are shown as gray, orange, and red colours, respectively [7].

Solvothermal synthesis

Solvothermal synthesis is the most common method for producing COFs [25]. Solvothermal synthesis takes 2–9 days and usually involves temperature (80–120 °C) within a closed container with an ideal pressure of 150 mmTorr before the reaction system is enclosed inside a 10 cm³ vessel. However, scientists have synthesized a crystalline structure functional SiCOF5 at a higher temperature of 180 °C [26]. SiCOF-5 was made by reticulating dianionic hexacoordinate [SiO6]²⁻ nodes comprising triangular triphenylene construction units with a Na₂[Si(C₁₈H₆O₆)] molecular structure. (Where C₁₈H₆O₆ stands for triphenylene-2,3,6,7,10,11-hexakisolate) (Figure 4). Nanocrystals COFs were generated after four days of combining 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and methyltrimethoxysilane (MTMS) in a sealed vessel. The substance's porosity (BET surface area) and thermal stability were found to be 370 m²g⁻¹ and 500 °C, accordingly [26].

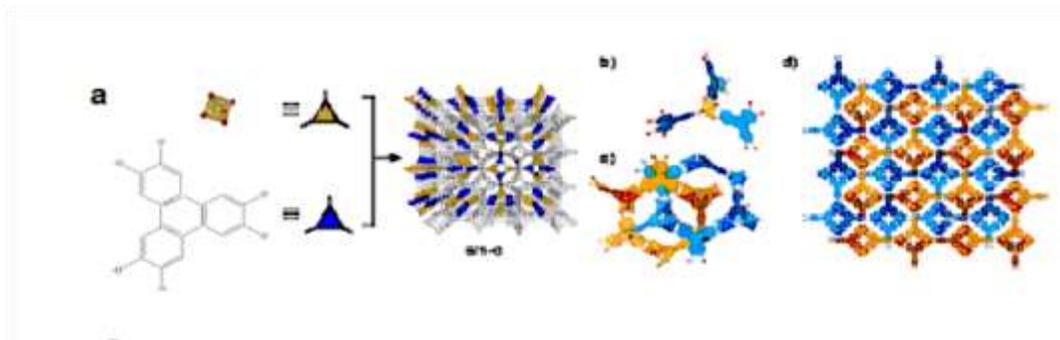


Figure 4. (a) The underlying net of SiCOF-5 is composed of triangular Si(O₂)₃ dianions (yellow triangles) linked via triangular deprotonated HHTP building blocks (blue triangles). The resulting augmented net is a doubly interpenetrated 3-csrs-c net. Schematic representation of a guest-free SiCOF-5 framework (d) composed of SiO₆ and triphenylene nodes (b) extending in two interpenetrated nets (c). extra-framework cations are omitted for clarity reasons [26].

The solvents used to make COFs is very important since it controls reactant solubility and has a significant link with reaction rate [27] crystal nucleation, crystal growth rate, and selfassembly. As a consequence, selecting the best solvent system for obtaining crystalline COFs has been a difficult task for a long time [9]. A co-solvent combination was commonly utilized to generate COFs in the existence of an acidic catalyst. Solvent assortments such dioxanemesitylene [7], dioxane-toluene [11], Dimethylacetamide-o-dichlorobenzene [28], and Tetrahydrofuran-methanol [29] were utilized to produce COFs materials. A solvent blend of dioxane and ethanol was applied to developed imine-linked COFs, and a ternary solvent logic was used to synthesize COF materials, in which a mixture of N-methyl-2-pyrrolidone (NMP), mesitylene, and isoquinoline generated high yields of crystalline PI-COF-4 and PI-COF-5 after five days of process [15,30]. Mono solvents were proven to be effective in the production of crystalline COFs, as illustrated by COF-DL229, a 3D COF. The tetrahedral 1,3,5,7-tetrakis(4aminophenyl)-adamantane (TAPA) and linear 1,4-phthaldehyde (PTA) were integrated into a single solvent, 1,2-dichlorobenzene [31]. The thermodynamic control process also requires a suitable concentration of building components or catalysts [27]. Scientists created a reflux method for producing COF substances by condensation of benzene-1,3,5-triboronic acid (BTBA) with 1,2,4,5-tetrahydroxybenzene (THB) [29]. This procedure was simple to evaluate and

produced a COF-18 composite with a surface area of $1260 \text{ m}^2\text{g}^{-1}$ and a pore volume of $0.29 \text{ cm}^3\text{g}^{-1}$ in 3 days without the usage of enclosed containers.

Ionothermal Synthesis

Ionothermal synthesis is the method of producing substances with ionic liquids as a solvent as well as a potential framework or pattern controlling tool. The technique is similar to hydrothermal; however, the solvent is water instead of steam. Ionic liquids (ILs) have gained a lot of attention from a number of different industries [32]. The body of research concentrated on the compounds' potential for "green" chemistry, with an emphasis on the effort to substitute organic solvents in homogeneous catalysis [33]. These synthetic activities are often performed at high temperatures, leading to the establishment of solid layer materials. Alkali metal hydroxide molten composites, for example, can be utilized as the molten stage in the synthesis of various inorganic solids, and are frequently confined in inert vessels (such as silver). Molten salt synthesis methods, in particular, are utilized to completely replace established solid phase synthesis procedures [34]. The current interpretation of ionic liquids, on the other hand, usually concentrates on materials that are liquid at low temperatures and include organic molecules. Several 3D COFs were synthesized using ionic liquids as a reaction solvent. a team of researchers who initiated the approach [35]. Under exceedingly mild circumstances, crystalline 3D COFs were produced. 3D-IL-COF-1 (Figure 5), was acquired in less than 3 minutes, indicating a quick reaction. It was also observed that the ionic liquid might be regenerated without losing its effectiveness. This research not only established a novel method for synthesizing COFs, but it also paved the path for the production of green large-scale COFs in industry.

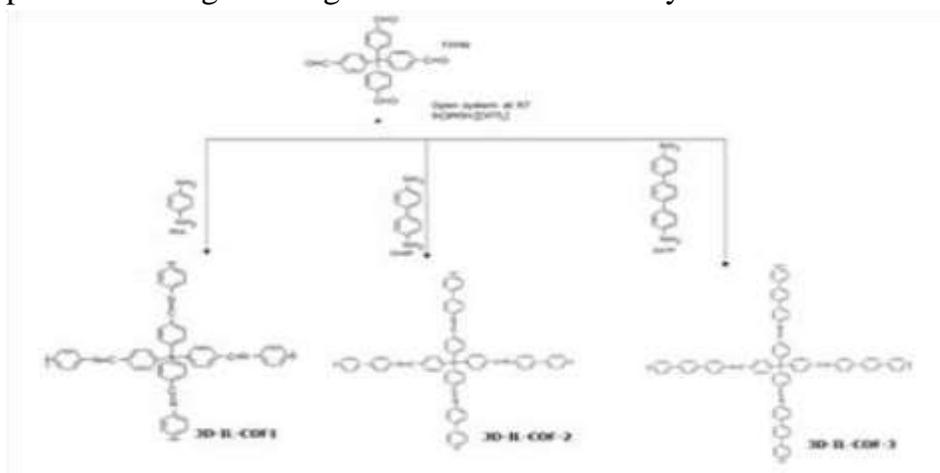


Figure 5: Schematic representation of the synthesis of 3D ionic liquid-containing (3D-ILCOFs). Condensation of tetrahedral tetrakis(4-formylphenyl)methane (TFPM) and three expanded linear links, p-phenylenediamine (PDA), 4,4'-diaminobiphenyl (DABP), and 4,4''diamino-p-terphenyl (DATP), to give a series of 3D-IL-COFs based on the open system at room temperature by using [BMIm][NTf₂] as green solvent [35].

Microwave Synthesis

TpPa-COF-1 was obtained by a condensation between p-phenylenediamine (Pa) and 1,3,5-triformyl-phloroglucinol (Tp) under standard solvothermal environments [36] of (2–3 days) and high-temperature (120 °C), yielding TpPa-COF-1 with a good yields (60–80 %) in a conventional solvothermal method.. In 2015, scientists microwave synthesized TpPa COF-1- by forming a 3:2 molar ratio TP solution in a mixture of mesitylene/1,4-dioxane/3 M acetic acid (3: 3: 1) in a glass microwave tube and microwave irradiation heated at 100 °C with stirring for 60 minutes utilizing microwave synthesized TpPa COF-1 [37]. The TpPa-COF-1 produced after the work yielded 83 % and had attributes identical to COF produced by normal solvothermal synthesis. As a consequence, the microwave technique means that effective and clean completion of the synthetic process, bringing up new possibilities for larger-scale applications [9]. Due to the lack of a sealed vessel in microwave synthesis, the microwave solvent extraction procedure effectively eliminates pollutants and impurities contained in the structures, allowing for higher porosity. The solvothermal approach could be totally replaced by microwave technology [10,21].

Characterization of COFs

COFs have a similar characterization profile to crystalline MOFs, but are more complex. The architectural regularity, atomic interconnection, porosity, and morphology of COFs are all critical factors to consider when analysing them. When it comes to MOF structures, it is quite common to produce appropriate single crystals and subject them to single crystal X-ray diffraction for structural identification. The second technique for analysing the structures on COF materials is powder X-ray diffraction (PXRD). However, evaluating structural design using collected PXRD marks is exigent and entails the use of computational simulation software. [38]. The Pawley and Rietveld approaches

are used to optimize observable PXRD trends in order to efficiently construct the unit-cell lattice. Additionally, the average pore size determined from isotherm gas absorption data may provide strong support for the preferred COF structures. Additionally, a comparison of measured and estimated densities may aid in indicating the desired COF structures [13]. Apart from structural regularity, atomic connectivity in COFs materials, particularly for the newly formed covalent bonds, is an effective characterization requirement. There is no doubt that solid-state NMR spectrometry is a powerful technique that has been successfully used to classify a variety of other solid materials, including zeolites, organic polymers, and MOFs [3]. The majority of the atoms in COF structures, such as ^1H , ^{13}C , ^{11}B , ^{15}N , ^{29}Si , and ^{17}O , have nuclear spin (I), making NMR effective for them. Those with nuclear spin $I = 1/2$, such as ^{13}C , ^{15}N , and ^{29}Si may benefit from a combination of the traditional magic-angle spinning (MAS) NMR technique and crosspolarization (CP) or high-power proton decoupling (HPDEC). Due to the low natural abundance of the ^{15}N isotope, the use of ^{15}N -enriched building units for COF synthesis is usually appropriate for ^{15}N MAS NMR measurements. While ^1H also exhibits nuclear spin $I = 1/2$, the ^1H MAS NMR spectra are less informative due to the strong homonuclear dipole-dipole interactions. FTIR spectroscopy originally used for theoretical and practical study of organic materials, offers extensive reports on chemical composition, chemical bonding, and the molecular system. SEM microscopy is used to examine the morphology of COF products (SEM). In considerations of microscopic examination, standard SEM analysis usually has a resolution of a few tens of nanometers, which is more than enough for a fair assessment of morphology and size in most circumstances. Vital information on crystalline size and shape can be obtained via optical microscopy. , imaging such as charged effects can often distract from, or entirely impede, the capture of high-quality SEM images [39]. The most typical solution is to coat the samples with a superconductor (e.g., gold, platinum or osmium) to reduce charge accumulation from the electron gun. The elemental composition investigation is based on the identification of distinctive X-rays released by the sample's surface layers, which is known as energy-dispersive X-ray analysis (EDX). Whereas the thickness of the layer examined by EDX vary based on material and equipment variables, this examination is mostly confined to the interface and is semiquantitative [40].

Conclusion

This study summarizes and discusses recent documented developments in the design principles, synthesis and characterization of crystalline porous COFs products. Until now, the primary hurdle in COF processing has been the development of efficient COF substances with extremely robust and regular structures. While the produced COFs may exhibit reasonable PXRD trends due to their low crystallinity, the ultimate architectural predictability is indeed low in certain situations. Theoretical patented predictions on electronic adsorption bands, bandgap, ion conduction, and charging-carrier stability are indispensable and can provide useful input on the structural architecture of COFs. Analytical approaches that are applicable to the representation or resolution of eclipsed or slipped stacking systems are difficult to find. This can be addressed through the development of single-crystal COFs. With current strategies, the ability to improve surface areas and porosities is extremely limited; thus, the development of new techniques and skeletons capable of significantly enhancing these attributes is critical for achieving several COF applications.

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