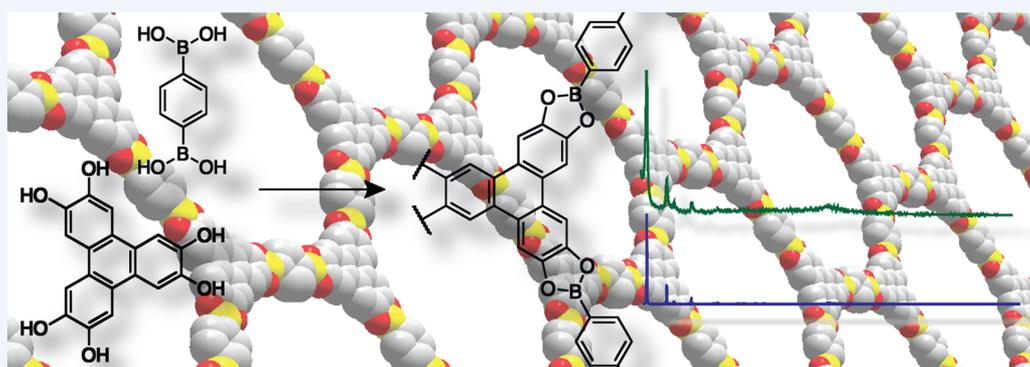


Chemistry of Covalent Organic Frameworks

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CONSPECTUS: Linking organic molecules by covalent bonds into extended solids typically generates amorphous, disordered materials. The ability to develop strategies for obtaining crystals of such solids is of interest because it opens the way for precise control of the geometry and functionality of the extended structure, and the stereochemical orientation of its constituents. Covalent organic frameworks (COFs) are a new class of porous covalent organic structures whose backbone is composed entirely of light elements (B, C, N, O, Si) that represent a successful demonstration of how crystalline materials of covalent solids can be achieved. COFs are made by combination of organic building units covalently linked into extended structures to make crystalline materials. The attainment of crystals is done by several techniques in which a balance is struck between the thermodynamic reversibility of the linking reactions and their kinetics. This success has led to the expansion of COF materials to include organic units linked by these strong covalent bonds: B–O, C–N, B–N, and B–O–Si.

Since the organic constituents of COFs, when linked, do not undergo significant change in their overall geometry, it has been possible to predict the structures of the resulting COFs, and this advantage has facilitated their characterization using powder X-ray diffraction (PXRD) techniques. It has also allowed for the synthesis of COF structures by design and for their formation with the desired composition, pore size, and aperture. In practice, the modeled PXRD pattern for a given expected COF is compared with the experimental one, and depending on the quality of the match, this is used as a starting point for solving and then refining the crystal structure of the target COF. These characteristics make COFs an attractive class of new porous materials. Accordingly, they have been used as gas storage materials for energy applications, solid supports for catalysis, and optoelectronic devices. A large and growing library of linkers amenable to the synthesis of COFs is now available, and new COFs and topologies made by reticular synthesis are being reported. Much research is also directed toward the development of new methods of linking organic building units to generate other crystalline COFs. These efforts promise not only new COF chemistry and materials, but also the chance to extend the precision of molecular covalent chemistry to extended solids.

■ INTRODUCTION

The chemistry of linking molecular building blocks by strong covalent bonds to make crystals of extended structures, reticular chemistry, has yielded several new classes of porous materials among which covalent organic frameworks (COFs) are the most recent example.^{1–3} On a fundamental level, the directionality of covalent bonds provides a means of controlling how building units come together into pre-designed structures. These advantages, combined with the strength of the linkages, lead to robust materials, which could be exploited in various applications, including gas storage and separation, catalysis, and

electronics. The challenge in assembling materials in this way is to overcome the “crystallization problem”: the linking of molecular building blocks by strong covalent bonds often yields amorphous or poorly defined materials. This problem has been addressed fruitfully in making COFs through the formation of B–O, C–N, B–N, and B–O–Si linkages.^{1,4–6} In this Account, we outline how this chemistry was used to make crystalline COFs and highlight their synthesis, characterization, and properties.

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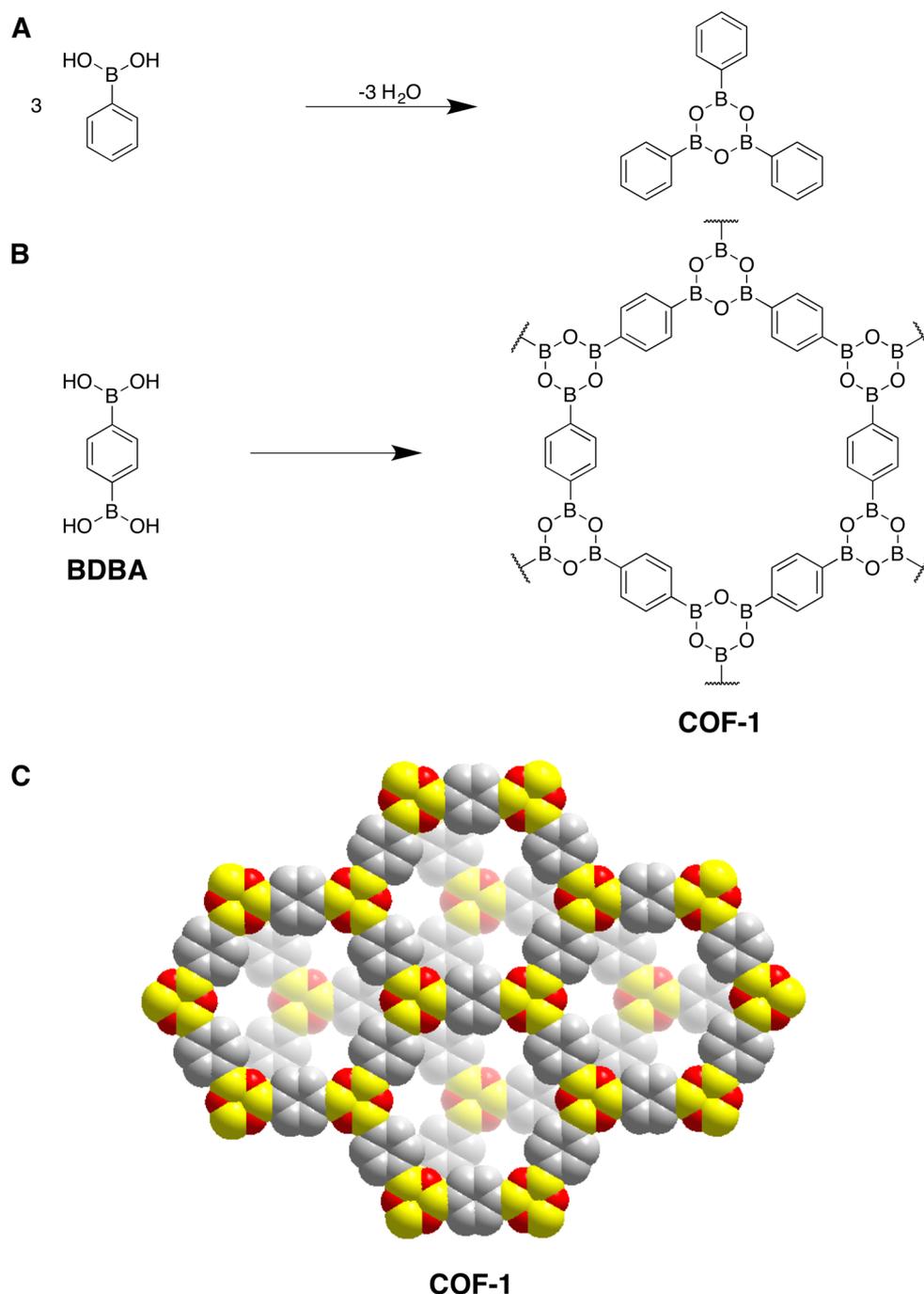


Figure 1. Self-condensation of boronic acid to form COFs. (A) Example of molecular condensation reaction to generate boroxine anhydride ring. (B) Structure of one pore of COF-1. (C) Space-filling diagram of the powder X-ray crystal structure of COF-1, viewed along the *c* axis. Carbon, boron, and oxygen are gray, yellow and red, respectively. Hydrogen atoms are omitted for clarity.

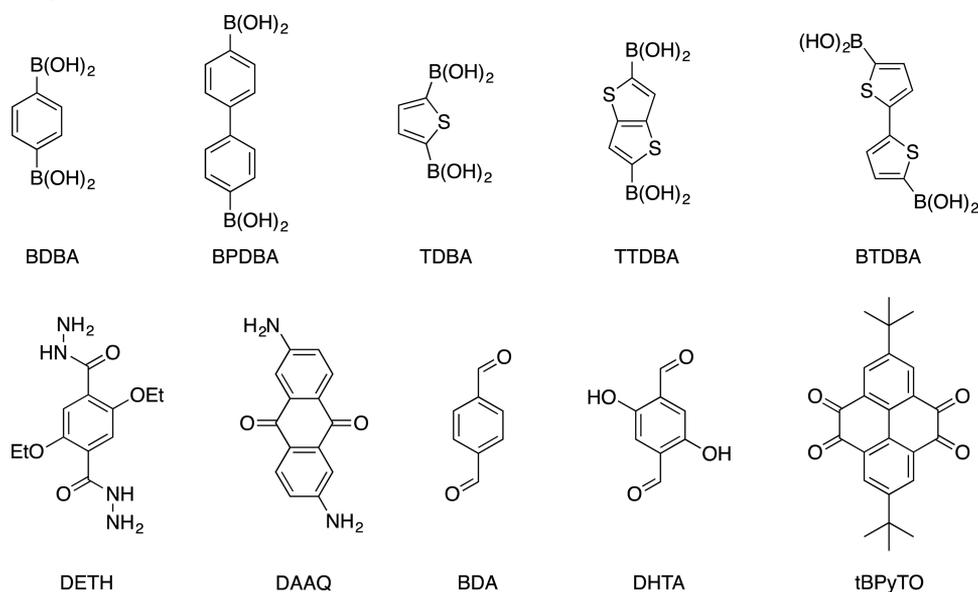
THE CRYSTALLIZATION PROBLEM

In principle, the formation of dense noncrystalline solids by linking building units is expected to be thermodynamically favorable. For example, amorphous cross-linked polymers,⁷ discussed further below, can be readily obtained by the linkage of organic building units with strong bonds; however these materials lack both the short- and long-range order that provide the precise structural characterization and control offered by crystalline materials. In order to afford an extended crystalline solid, the formation of linkages should be reversible and the reaction rates must be on a time scale that allows for self-correction of

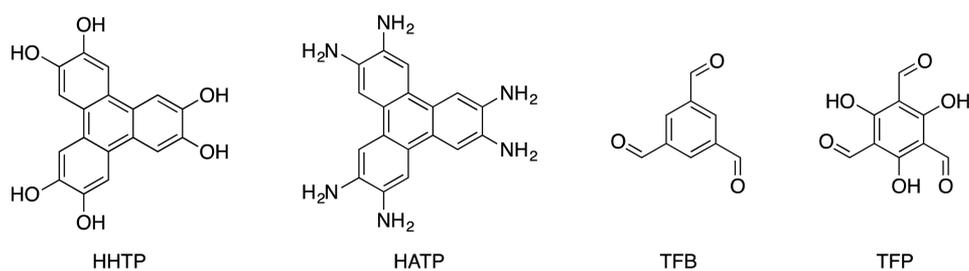
defects. Using covalent bonds as linkages presents a special crystallization challenge because of their tendency to form irreversibly under mild conditions. Thus, it is important to find the conditions under which reversible bond formation is possible without resorting to extreme temperatures or pressures. In COF chemistry, this goal was initially realized by using condensation reactions where stoichiometric quantities of a small molecular byproduct (e.g., water) are generated. Conveniently, this allows for the modulation of the reaction's equilibrium simply by controlling the amount of this species in the system. In practice, this is accomplished by either using solvents where the byproducts have limited solubility or

Scheme 1. Linkers Discussed in This Account

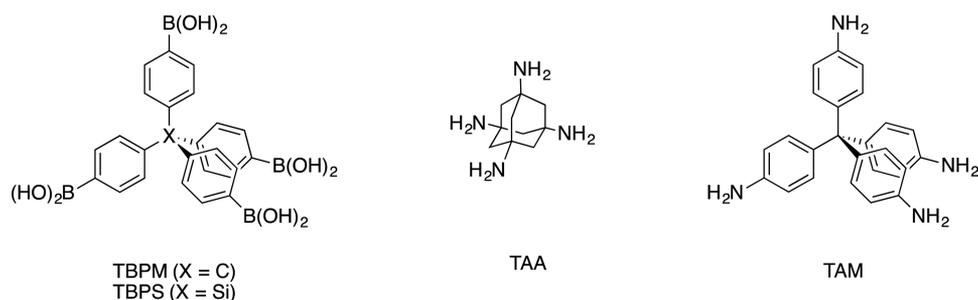
Ditopic Linkers



Tritopic Linkers



Tetratopic Linkers



through controlling the pressure in the vessel. In the section that follows, we provide examples of how covalent chemistry performed on molecular building units can be translated to extended structures by linking such units into crystalline two- and three-dimensional COFs.

LINKING ORGANIC BUILDING BLOCKS INTO COFs

COFs were first synthesized by the self-condensation of boronic acids to produce boroxine anhydride-based linkages in the form of B_3O_3 rings (Figure 1A). In this way, COF-1 was prepared as a crystalline material by the self-condensation of 1,4-phenylenediboric acid (BDBA) (Figure 1B; note that line drawings of organic building units referred to in this contribution are shown in Scheme 1) to produce a structure consisting of extended layers stacked in staggered form to give

hexagonal pores with 15 Å diameter and a BET surface area of $711 \text{ m}^2 \text{ g}^{-1}$ (Figure 1C).¹ Control of the headspace in the sealed reaction tube modulated the amount of water and therefore the reversibility of the condensation reaction to ultimately crystallize the COF. This method has also been applied to the synthesis of three-dimensional structures, by condensation of molecules with tetrahedral geometry, such as TBPM or its silane analog TBPS.⁸

In addition to self-condensation, boronic acids can also react with catechols to form boronate esters (Figure 2A), as in the case of COF-5 and the three-dimensional porous structure COF-105,^{1,8} or with silanols to form borosilicate bonds, as in the case of COF-202.⁶ In one important case, COF-108 was prepared through the reaction between HHTP and TBPM (Figure 2B) to produce a material with three-dimensional pores

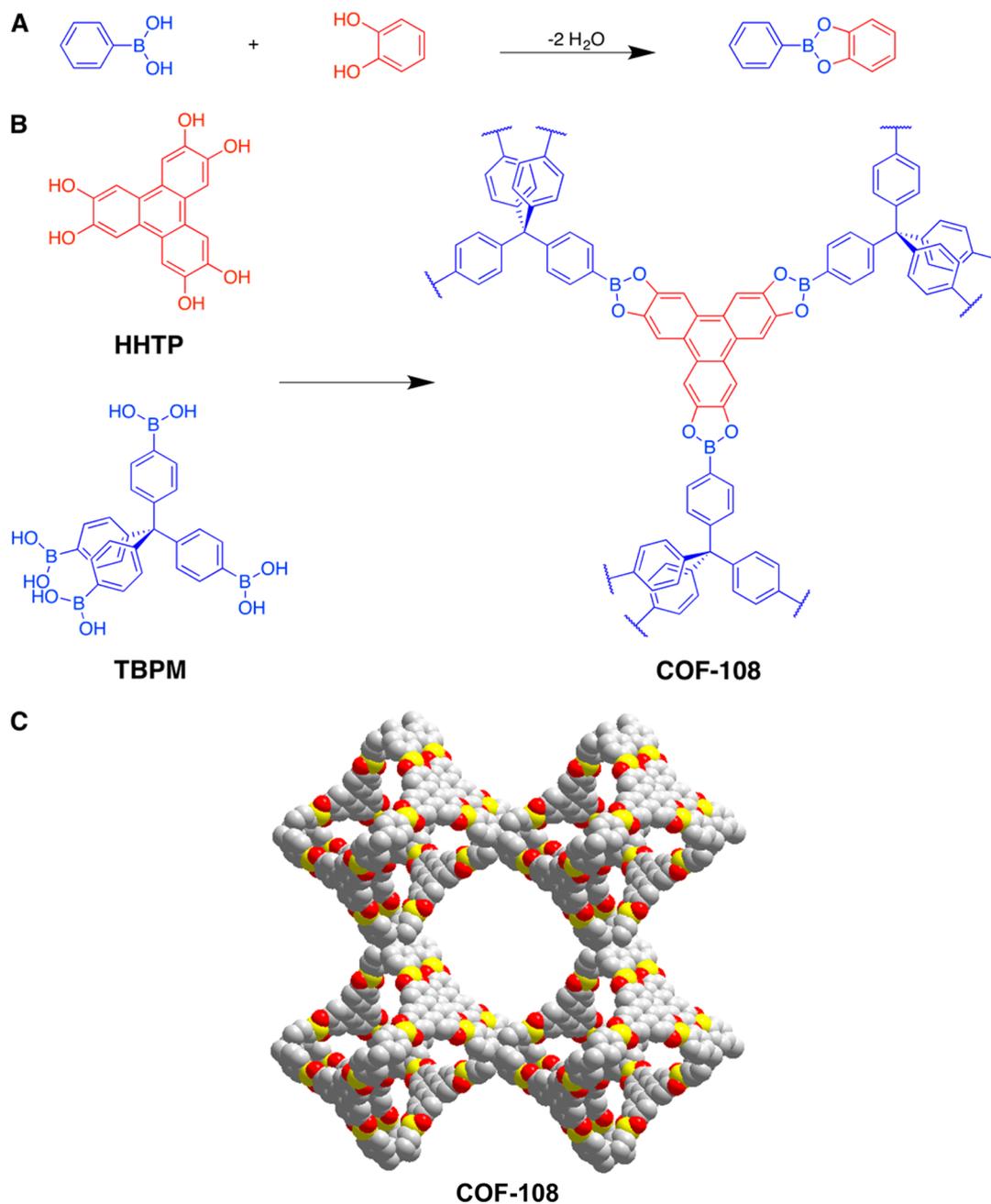


Figure 2. Boronate ester linkages used in the synthesis of COFs. (A) Example of molecular condensation to form boronate ester. (B) Structure of a fragment of COF-108. (C) Space-filling diagram of the powder X-ray crystal structure of COF-108. Carbon, boron, and oxygen are gray, yellow, and red, respectively. Hydrogen atoms are omitted for clarity.

and an extremely low density of 0.17 g cm^{-3} (Figure 2C).⁸ This synthetic route is remarkably general in scope and has been applied to a large array of boronic acids. For example, isorecticular series of layered COFs with hexagonal⁹ or square¹⁰ topologies have been reported. This resulted in families of related materials of systematically increased pore sizes, reaching pore apertures as large as 4.7 nm.

COFs have also been synthesized through the formation of C–N bonds. The first example, COF-300,⁴ is linked by imine condensation of aldehyde and amine linkers (Figure 3A). This material was made by the reaction between TAM and BDA (Figure 3B), resulting in a framework with a 5-fold interpenetrated dia topology^{11,12} and a BET surface area of $1360 \text{ m}^2 \text{ g}^{-1}$ (Figure 3C). Again, the key to obtaining a

crystalline solid was the use of a sealed reaction vessel, which allowed for modulation of the reaction's equilibrium. Similar to boronic acid condensations, the formation of imine bonds has proven to be a versatile strategy for the synthesis of COFs, and numerous materials have subsequently been prepared with this same reaction.^{13,14} A similar strategy was pursued to enhance the chemical stability of imine-based COFs where the reversible Schiff base formation is followed by irreversible tautomerization of the intermediate enol-imine form to the keto-enamine species.¹⁵ The materials prepared by this route have shown remarkable stability in acidic and basic media.

Similarly, C–N bond formation has been applied to COFs with hydrazone linkages.¹⁶ These materials are prepared through

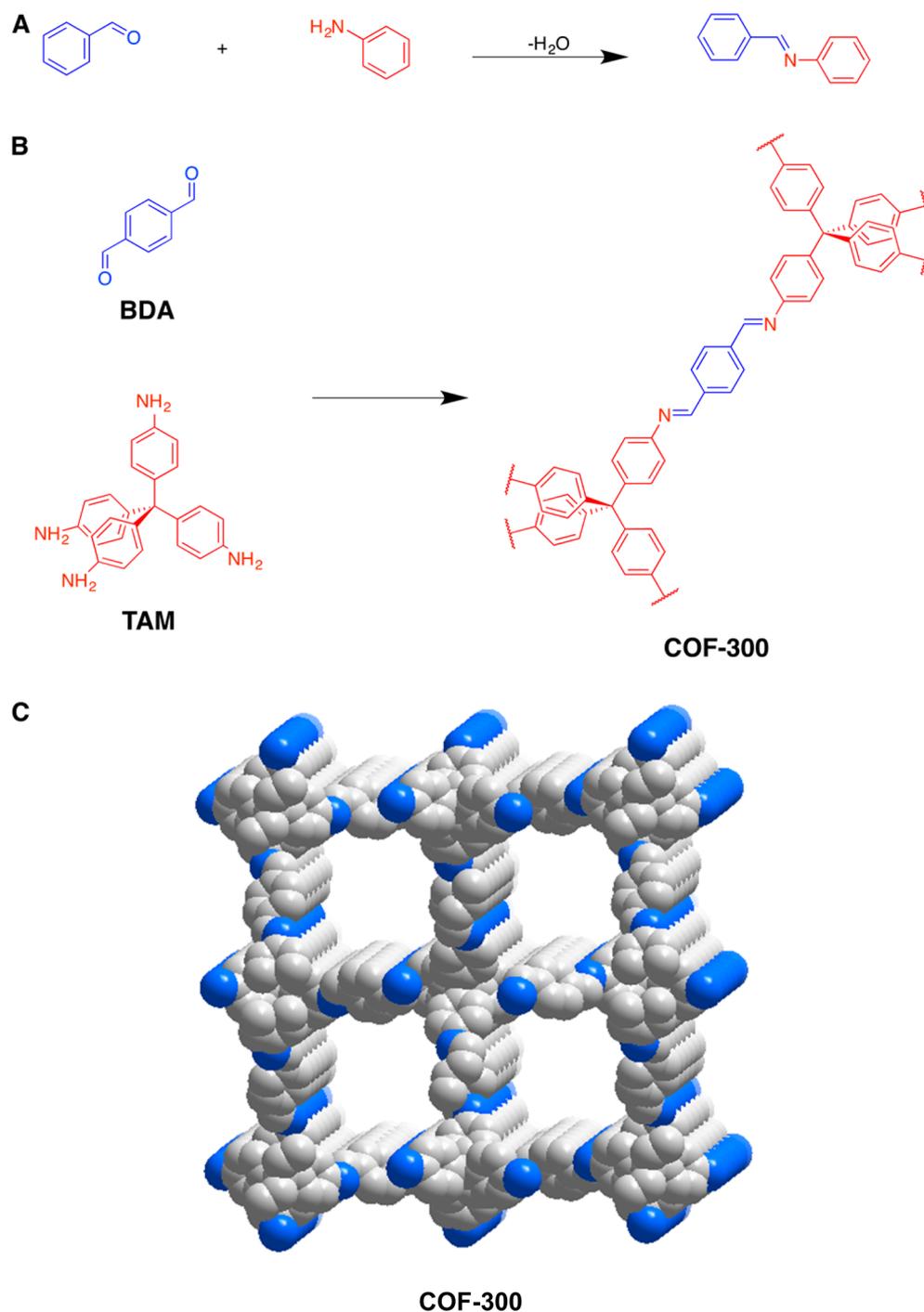


Figure 3. Application of imine bond formation to COFs. (A) Example of molecular condensation to form imine bonds. (B) Structure of a fragment of COF-300. (C) Space-filling diagram of the powder X-ray crystal structure of COF-300. Carbon and nitrogen are gray and blue, respectively. Hydrogen atoms are omitted for clarity.

the condensation of aldehydes with hydrazide building blocks (Figure 4A). COF-42 and COF-43 are the first two examples of hydrazone COFs. COF-42 was formed from the reaction of DETH and TFB (Figure 4B). This produced a layered structure (Figure 4C) of hexagonal pores (28 Å in diameter) and a BET surface area of $710 \text{ m}^2 \text{ g}^{-1}$. This class of materials offers generally higher chemical stabilities than imine-based COFs. In particular, these linkages are less prone to hydrolysis and thus form more robust frameworks.¹⁷

Other COFs prepared with C–N bonds include those using azine linkages and those incorporating triazine rings. In the first

case, azine bonds are formed by the reaction between hydrazine and aldehyde building units.¹⁸ The triazine linkage is made under ionothermal conditions in molten ZnCl_2 by nitrile cyclotrimerization.¹⁹ More recently, the imidization reaction has also been successfully employed to synthesize polyimide COFs with high thermal stability.²⁰

The formation of B–N bonds has also been recently employed to prepare COFs through the synthesis of borazine ring linkages, which was achieved by decomposition of amineborane-functionalized building units.⁵

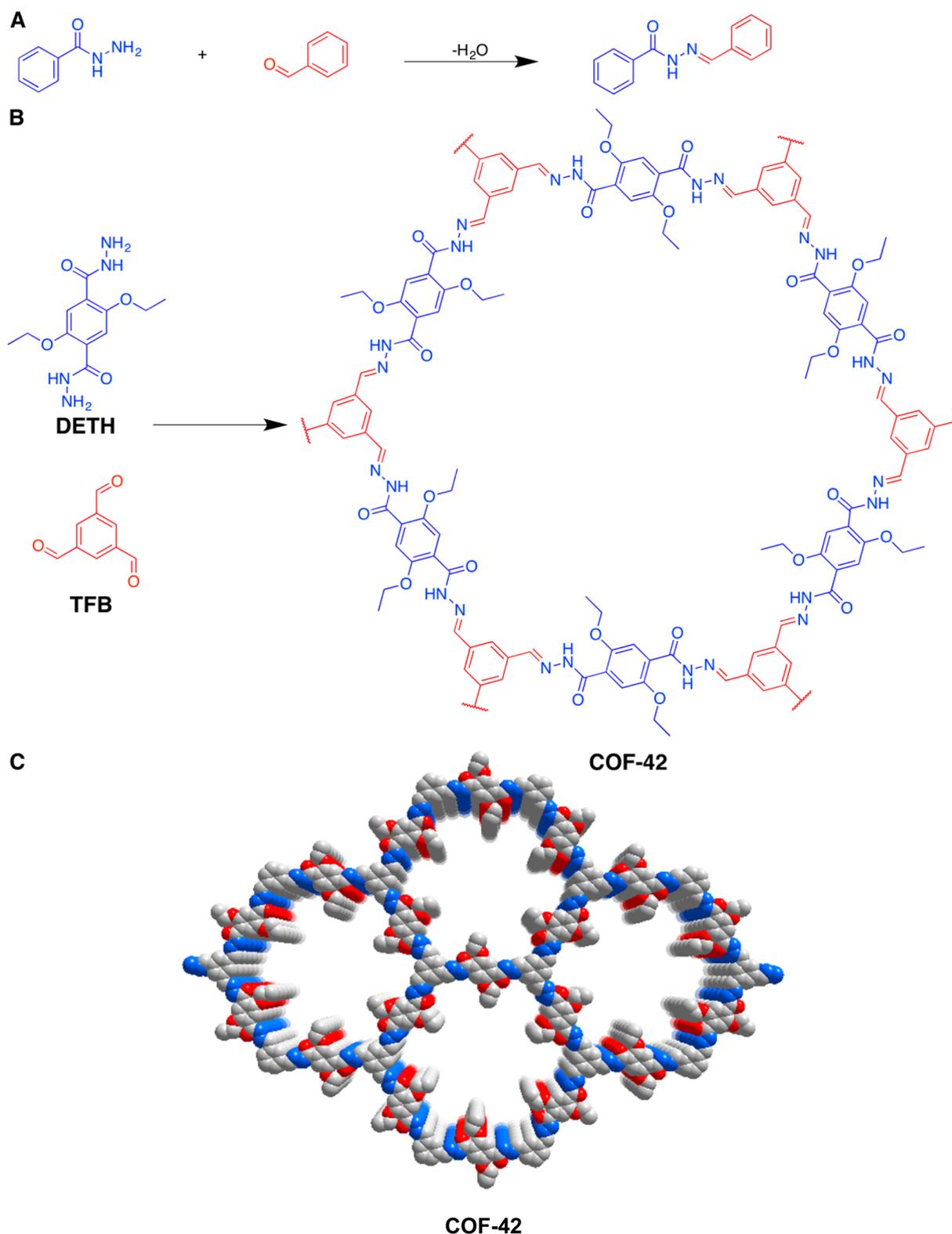


Figure 4. Application of hydrazone bond synthesis to COFs. (A) Example of molecular condensation to form a hydrazone. (B) Structure of one pore of COF-42. (C) Space-filling diagram of the powder X-ray crystal structure of COF-42. Carbon, oxygen, and nitrogen are gray, red, and blue, respectively. Hydrogen atoms are omitted for clarity.

COF STRUCTURES BY DESIGN AND THEIR CHARACTERIZATION

The fact that the building units used in the assembly of COFs maintain their geometry during the reaction makes it possible to predict the structure of the resulting solid. Using the symmetry

hypothesis where the most symmetric structures are more likely to result from such syntheses, it is straightforward to come up with a small number of expected structures from a large number of possibilities based on the geometry of the starting building units.^{11,12} The powder X-ray diffraction (PXRD) patterns

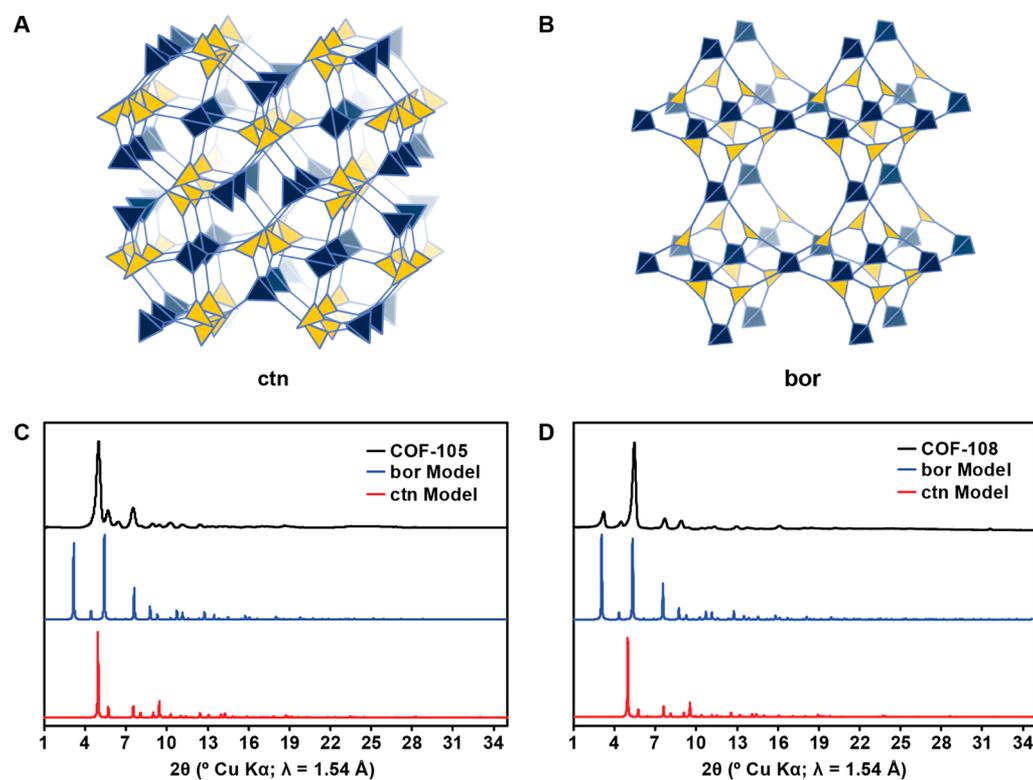


Figure 5. Structural elucidation through modeling. (A, B) Idealized **ctn** and **bor** topologies as the most symmetric possibilities for the assembly of tetrahedral and trigonal building units, respectively. (C, D) Experimental PXRD patterns obtained for COF-105 and COF-108 (black), respectively, and calculated patterns for crystal models based on **bor** and **ctn** (blue and red) topologies.

calculated for the expected structures are compared with the experimental patterns to confirm the correctness of the prediction. COFs represent the best examples of making materials by design, because it would not be possible to solve such crystal structures without prior knowledge of the expected outcome of the reaction.

For example, it is known that the combination of tetrahedral and triangular building units preferentially generates **ctn** or **bor** networks (Figure 5A,B, respectively). COF-105 and COF-108 are constructed by joining triangular HHTP with tetrahedral building units TBPM or TBPS, respectively.⁸ To determine the topologies of each COF, calculated models based on the **bor** and **ctn** networks were constructed by placing the TBPM or TBPS units at the tetrahedral nodes and the HHTP linkers at the triangular nodes, followed by geometry optimization along with energy minimization. The comparison of the simulated PXRD patterns with the experimental data indicates that COF-105 exhibits the **ctn** topology, while COF-108 assumes the **bor** topology (Figure 5C,D).

While this approach has been successful in the structural elucidation of COFs, it has many of the limitations associated with powder diffraction techniques. For example, PXRD patterns give little information about the stacking sequence of layers in two-dimensional COFs. In fact, the possibility of various layer-stacking sequences was recognized in the first COF report.¹ In the case of layered materials, the two extreme situations, staggered and eclipsed, are typically modeled. Other intermediate scenarios, such as inclined stacking, have been proposed based on energy minimization studies.²¹ It is worth noting that in contrast to the strong bonds making up the layers, the interactions between them are weak and therefore are not subject to the predictability found in reticular chemistry.

This limitation also applies to interpenetrated COFs, where the interpenetration number is often ambiguous and cannot always be derived definitively from the powder diffraction patterns. In these cases, geometrical and topological considerations might help in determining the degree of interpenetration. However, elucidation of a COF structure goes beyond PXRD methods and involves a host of solid-state characterization techniques. For instance, the completeness of the reaction between the linkers of COFs can be verified by FTIR and solid-state NMR spectroscopy, while gas sorption measurements are valuable in determining pore volume and size. All of these techniques, taken together, can provide a holistic picture of the structure.¹

Since large COF single crystals remain rare, diffraction techniques applicable to submicrometer sized samples provide a possible alternative. For instance, electron diffraction is applicable to the study of nanosized crystals because electrons interact more strongly with matter than X-rays. This technique already shows promise for COF structural elucidation. The use of electron diffraction allowed for the determination of the first single crystal structure of a COF, COF-320,²² which has 9-fold interpenetrating **dia** frameworks. For this study, the rotation electron diffraction (RED) technique²³ was applied, which allows for three-dimensional reconstruction of the reciprocal diffraction space by exposing a crystal to a rotating electron beam at varying angles. With this technique, a COF crystal with a minimal dimension of about 200 nm was sufficient to solve the structure. Given such a large number of interpenetrating frameworks, it would have been difficult to determine the structure using only calculated models and PXRD analysis, as explained above for other COFs.

■ PROPERTIES AND APPLICATIONS OF COFs

Porosity and Gas Storage

COFs' unique combination of crystallinity and organic functionality provide these materials with a variety of useful properties. As a first example, porosity is one of the most studied characteristics of COFs. They have been repeatedly shown to be permanently porous by measurement of gas sorption isotherms. Their pore size is also highly tunable, and COFs with micropores and mesopores have been reported.

In two-dimensional layered structures, porosity emerges from the formation of channels that run along the stacking direction. The channel diameters can be finely tuned by judicious selection of linkers. For example, COF-1 has a structure based on hexagonal layers that stack in a staggered fashion (**gra** topology), producing a 7 Å pore aperture. Isoreticular expansion of this COF produced frameworks consisting of eclipsed layers (**bnn** topology) containing hexagonal channels with pore diameters ranging from 27 Å (COF-5) to 47 Å (HHTP-DPB COF).^{1,10} Similarly, layered COFs with square channels have been reported, formed from porphyrin- or phthalocyanine-derived linkers and using imine and boron ester linkages.^{24,25} Furthermore, such layers stack in an eclipsed fashion, producing square pores with diagonals as large as 44 Å, some of which have also been formed as thin films.²⁶

Their large surface areas and low densities make COFs promising for use in gas storage applications. COFs have exhibited high capacities for the storage of important gases such as methane, hydrogen, and carbon dioxide.²⁷ In particular, COFs have proven to be exceptional methane storage materials, even at room temperature. In general, three-dimensional COFs have exhibited the largest storage capacities, which can be related to their high surface area and pore volumes compared with layered materials. For example, the three-dimensional non-interpenetrating COF-102, with a Langmuir surface area of 4650 m² g⁻¹, has a methane storage capacity of 25 wt % at 298 K and 80 bar (203 cm³ cm⁻³). Under identical conditions, even the 9-fold interpenetrating COF-320 exhibits high methane uptake with a 15 wt % capacity (176 cm³ cm⁻³).

Due to its importance in clean energy, large efforts have been devoted to finding materials with high hydrogen storage capacities, and COFs have also been evaluated for this purpose. COF-102 and COF-103 show the largest hydrogen storage capacity among all reported COFs, with hydrogen uptake values of 72.4 and 70.5 mg g⁻¹, respectively, at 77 K and 85 bar. These values are similar to those reported for the highest performing MOFs.²⁷ Incorporation of metal sites into COFs has been proposed as a method to increase the interaction strength between the adsorbent and the hydrogen molecules and thus improve the room temperature storage capacity. Indeed, calculations indicate that metalation of COF-301 with PdCl₂ produces COF-301-PdCl₂, a material that would exceed the DOE target for hydrogen storage at room temperature.²⁸ This framework is formed through imine condensation of the tetrahedral TAM and DHTA linkers to generate multiply interpenetrating **dia** frameworks. The unique feature of this COF is the hydroxyl groups adjacent to the imine linkage, which generate bonding sites for metal centers. Hybrid DFT functionals were used to estimate the interactions between H₂ molecules and the framework, and H₂ adsorption isotherms were simulated with grand canonical Monte Carlo calculations. The results of these models indicate that COF-301-PdCl₂ would be capable of storing up to 60 g L⁻¹ at room temperature and 100 bar.

COFs are also useful for the capture and storage of harmful gases. For instance, ammonia is a widely employed chemical that needs to be safely transported due to its toxicity and corrosiveness. As a Lewis base, ammonia can be effectively captured through interactions with Lewis acidic groups, such as the boron atoms present in boroxine or boronate ester based COFs. COF-10, formed by condensation of HHTP and BPDBA building units, shows high capacity (15 mol kg⁻¹) for ammonia storage.²⁹ Remarkably, there is no loss of capacity or crystallinity after three consecutive ammonia adsorption/desorption cycles.

Catalysis

The use of porous materials as heterogeneous catalysts is of great interest because they offer the advantages of conventional heterogeneous catalysis combined with greater accessibility of active sites. However, despite their high porosity and great tunability, the use of COFs in catalysis remains largely unexplored relative to other classes of porous materials. Two base-functionalized COFs, BF-COF-1 and BF-COF-2, have been recently used as catalysts in Knoevenagel condensation reactions with a variety of substrates.¹³ These materials are formed by imine condensation between TAA and either TFB or TFP to generate BF-COF-1 or BF-COF-2, respectively. The obtained materials exhibit high activity in the conversion of benzaldehyde to 2-benzylidenemalononitrile (96% and 98% for BF-COF-1 and BF-COF-2, respectively). Importantly, these two COFs have differing pore aperture sizes, resulting in modified selectivities.

While BF-COF-1 and BF-COF-2 have intrinsic activity, the catalytic species may also be introduced into the framework after its synthesis. For example, Pd(OAc)₂ was postsynthetically added into an imine-linked COF to generate Pd/COF-LZU-1.¹⁴ X-ray photoelectron spectroscopy data suggests that the Pd atom is fixed between two neighboring COF layers, coordinated to the nitrogen atoms of the framework. The material has exhibited high reactivity and good recyclability in Suzuki–Miyaura couplings. Similarly, a layered imine COF has also been used for the immobilization of gold nanoparticles, prepared by the solution infiltration method after the COF was synthesized. The resulting material shows high activity in the reduction of 4-nitrophenol to 4-aminophenol.³⁰ Finally, a catalytic system consisting of a hydrazone-based COF doped with platinum has recently shown activity in photocatalytic production of hydrogen.¹⁷ In this case, the COF acts as a photosensitizer for exciton generation, while platinum is the proton reduction catalyst.

Optoelectronics

The optoelectronic properties of COFs have also found use outside the field of catalysis. For example, TP-COF, synthesized from triphenylene and pyrene linkers, has shown semiconducting and luminescent properties.³¹ In addition, high charge carrier mobility has been measured in porphyrin-based COF-66 and COF-366.²⁴ These materials are ideal for this application because they adopt an eclipsed conformation with square channels and small interlayer distances. Both frameworks are hole conducting and have charge mobility values of 8.1 and 3.0 V⁻¹ s⁻¹ cm² for COF-366 and COF-66, respectively, values that are higher than those exhibited by common conducting polymers. Charge carrier mobility has also been demonstrated for phthalocyanine-based COFs²⁵ and for the highly conjugated CS-COF³² prepared by condensation of HATP with tBPyTO. In the latter case, the COF was mixed with C₆₀ to produce a donor/acceptor composite material, which exhibited excellent photoconductive properties. Finally, a COF capable of energy storage was prepared by the reaction of the redox-active anthraquinone building unit, DAAQ,

with TFP.³³ This framework exhibits a capacitance significantly higher than both non-redox-active COF materials and monomeric DAAQ, and this capacitance is maintained even after 5000 charge–discharge cycles.

Thin-Film COFs

Further research is being directed toward improving the use of COFs in optoelectronic applications. The synthesis of COF thin-films is a current goal in this area, and two approaches have been applied to this task. First, the material may be formed on a surface *in situ*. Second, the COF may be formed first and then deposited on a surface afterward. Applying the first strategy, COFs have been synthesized on a Ag(111) surface (Figure 6),³⁴ and on

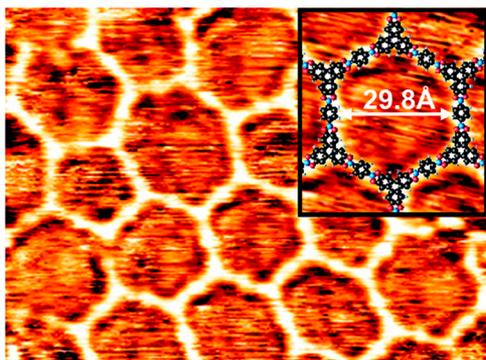


Figure 6. Scanning-tunnel electron microscopy image of COF-5 material grown on a Ag(111) surface. Reproduced from ref 34. Copyright 2008 American Chemical Society.

single layer graphene.^{26,35} In the second technique, a layered COF may be synthesized as a powder and then exfoliated to yield materials consisting of a limited number of sheets, which can be deposited onto a surface. Several methods have been reported, including sonication,³⁶ mechanical delamination,³⁷ or immersion³⁸ in appropriate solvents.

To further modify and improve the electronic properties of COFs, linkers with inherent electrical conductivity, such as thiophene derivatives, are also being explored. Two such COFs, prepared with TTDBA³⁹ or BTDBA⁴⁰ in combination with HHTP have been reported. To improve their electronic properties, these COFs were grown as thin-films on polycrystalline surfaces and then impregnated with fullerene derivatives to produce mixed donor/acceptor materials. An isorecticular series of COFs formed by condensation of TDBA, BTDBA, and TTDBA with HHTP has also been reported.⁴¹ The electron donor molecule tetrathiafulvalene has been incorporated into a layered imine-based COF as a powder and as an oriented thin film. Diffusion of electron acceptor dopants, such as iodine or tetracyanoquinodimethane into thin films of this material resulted in conductivity values as high as 0.28 S m⁻¹.

ORGANIC MATERIALS INSPIRED BY COFs

Although the scope of this Account is limited to crystalline COFs, here we briefly mention some related materials that share common features such as the use of well-defined building blocks (akin to those applied in COFs), organic composition, and permanent porosity. Porous organic polymers are built up from rigid organic monomers, and although these materials lack the crystallinity and precise structural control found in COFs, some have exhibited interesting properties, including high porosity or electronic conductivity. These materials have been formed by

Sonogashira–Hagihara,⁴² Suzuki–Miyaura,⁴³ Yamamoto,⁴⁴ or Eglinton⁴⁵ couplings. The resulting solids are typically highly stable, and some also have high surface areas. For example, PAF-1 (polyaromatic framework-1) exhibits a BET surface area of 5600 m² g⁻¹.⁴⁴ It was initially proposed that this high surface area implies a structure based on the *dia* topology, since the molecular precursors are tetrahedral. However, because the material is amorphous, it was later argued that a model based on amorphous silica may also explain its high surface area.⁴⁶ Due to their high porosity and chemical stability, these amorphous porous polymers have found use in various applications, including gas capture and separation. For example, functionalized versions of PAF-1 that incorporate sulfonyl groups, denoted PPN-6-SO₃E (porous polymeric network-6, E = H⁺, Li⁺, NH₄⁺), have demonstrated high selectivity in the adsorption of carbon dioxide.^{47,48} Recently, the ammonia uptake of a number of related porous materials incorporating Brønsted acid groups has been investigated.⁴⁹ It was found that BPP-5 (Berkeley porous polymer-5), a porous polymer functionalized with carboxylic acid groups, exhibits an ammonia uptake of 17.7 mol kg⁻¹ at 1 bar. We believe the synergy between the chemistry of COFs and the assembly of these polymers will continue to yield such amorphous materials with interesting properties.

OUTLOOK

COFs have emerged as an important class of materials because their backbone is built entirely from light elements (thus far, C, N, O, B, Si) held together by strong covalent bonds (B–O, C–N, B–N, and B–O–Si) to make robust porous materials having the advantages of predictable structures and tunable pore functionality and metrics. Since the crystallization problem has been overcome in COF chemistry, at least for simple condensation and nitrile trimerization reactions, a large variety of COF structures have been made and will continue to evolve in their diversity and complexity. Although small crystals suitable for single crystal electron diffraction can be obtained, we believe making larger crystals is still a challenge and one we expect is being investigated by researchers in the field. Such large crystals will be very useful in exploiting the electronic properties of COFs.

The future challenges pertain to extending this covalent chemistry to C–O, C–C, and other such strong bonds, which will provide access to a whole new area of useful materials not the least of which are new forms of carbon.

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Notes

The authors declare no competing financial interest.

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Peter J. Waller was born in Minnesota, United States, in 1992. He received his B.A. in Chemistry and Mathematics at St. Olaf College in 2014 and joined the Yaghi group at the University of California, Berkeley, the same year. He is currently a second-year graduate student in the group, and is interested in the development of new COF linkages.

Felipe Gándara received his Ph.D. from the Universidad Autónoma de Madrid, Spain, in 2009, working in the Instituto de Ciencia de Materiales de Madrid, CSIC. Following this, he joined the Yaghi group as a postdoctoral researcher at the University of California, Los Angeles, and then at the University of California, Berkeley, where he worked until 2014. After this, he began his current position in the Multifunctional and Supramolecular Materials Group at the Instituto de Ciencia de Materiales de Madrid, where he is now a *Fundación General CSIC - ComFuturo Researcher*.

Omar M. Yaghi received his Ph.D. from the University of Illinois—Urbana (1990). He was an NSF Postdoctoral Fellow at Harvard University (1990–1992). He has been on the faculties of Arizona State University (1992–1998), University of Michigan (1999–2006), and University of California, Los Angeles (2007–2012). His current position is the James and Neeltje Tretter Professor of Chemistry, University of California, Berkeley, and Faculty Scientist at Lawrence Berkeley National Laboratory. His work encompasses the synthesis, structure, and properties of inorganic compounds and the design and construction of new crystalline materials. He has shown that organic and inorganic molecules can be stitched together into extended porous structures to make metal–organic frameworks, zeolitic imidazolate frameworks, and covalent organic frameworks.

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NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on November 18, 2015, with an atom labeled incorrectly on a skeletal structure in Figure 1B. The corrected version reposted on November 25, 2015.