

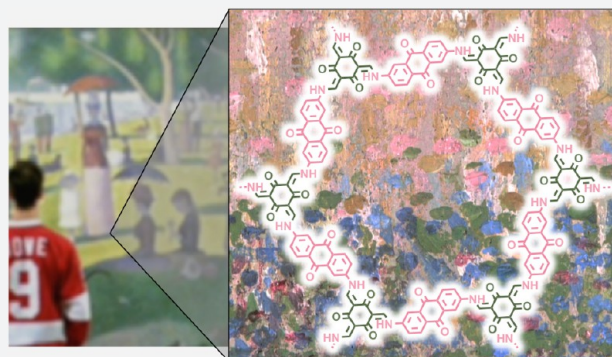
Covalent Organic Frameworks as a Platform for Multidimensional Polymerization

Ryan P. Bisbey^{†,‡} and William R. Dichtel^{*,†}

[†]Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

[‡]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States

ABSTRACT: The simultaneous polymerization and crystallization of monomers featuring directional bonding designs provides covalent organic frameworks (COFs), which are periodic polymer networks with robust covalent bonds arranged in two- or three-dimensional topologies. The range of properties characterized in COFs has rapidly expanded to include those of interest for heterogeneous catalysis, energy storage and photovoltaic devices, and proton-conducting membranes. Yet many of these applications will require materials quality, morphological control, and synthetic efficiency exceeding the capabilities of contemporary synthetic methods. This level of control will emerge from an improved fundamental understanding of COF nucleation and growth processes. More powerful characterization of structure and defects, improved syntheses guided by mechanistic understanding, and accessing diverse isolated forms, ranging from single crystals to thin films to colloidal suspensions, remain important frontier problems.



INTRODUCTION

In the painting *A Sunday Afternoon on the Island of La Grande Jatte*, neo-impressionist George Seurat depicts 17th century life by ordering dots of color across the canvas in a style known as pointillism. From afar the observer sees Parisians relaxing in the namesake park along the Seine, yet from a closer vantage one appreciates the synergy between paint and empty canvas, which blend to create vivid colors and shadows that merge into recognizable forms. The ability of chemists to approach this level of precision and collective function in organizing molecular species into two- or three-dimensional (2D or 3D) structures is only now emerging. The fields of molecular and polymer synthesis provide powerful and ever-expanding methods with outstanding chemoselectivity, stereospecificity, and control of polymer composition, size, architecture, and uniformity.¹ But polymerizing monomers into well-defined 2D or 3D structures is a historical gap that is now a rapidly developing frontier. Progress has come from several research areas, including supramolecular assembly,^{2,3} coordination chemistry,^{4,5} dynamic bond formation,^{6,7} topochemical polymerization,⁸ and advances in the characterization of nanostructured materials.⁹ These efforts are motivated by both fundamental interest and potential applications. 2D and 3D polymer networks offer unique structural features compared to established linear, branched, or amorphous network polymers and therefore have distinct properties. Channeling Seurat, much of their utility emerges from their ability to organize molecular building blocks into structures whose chemical composition and free volume are versatile and tailorable.

The synthesis of covalent organic frameworks (COFs) represents a powerful and general approach to access 2D and 3D polymer networks.^{10–14} COF monomers are designed using directional bonding principles established for supramolecular assemblies^{15–17} and coordination polymers,¹⁸ yet COFs are linked by covalent bonds that confer superior thermal and chemical stability. Monomer shape determines the dimensionality and topology of the network and defines pores that are usually retained after solvent removal. For example, a square planar monomer with reactive groups at each vertex combines with a linear difunctional monomer to form a 2D square lattice (Figure 1A). 3D COFs are derived from nonplanar monomers, such as a combination of tetrahedral and linear monomers that generates a diamondoid net (Figure 1B). In practice, 3D COFs often form such that congruent frameworks interpenetrate (Figure 1B inset), and 2D COFs stack to form layered structures similar to graphite (Figure 1A insets). Directly synthesizing or isolating single-layer 2D COFs without resorting to ultrahigh vacuum techniques is an important contemporary challenge.

COFs offer a combination of properties not found in other materials:

- **Modularity.** COF chemistry offers a platform for designed molecular assembly that has not yet been fully exploited.^{19,20} Recent systems incorporate monomers with reduced symmetry,²¹ multiple monomer components with differing lengths,²² or more than one bond-

Received: March 22, 2017

Published: May 19, 2017

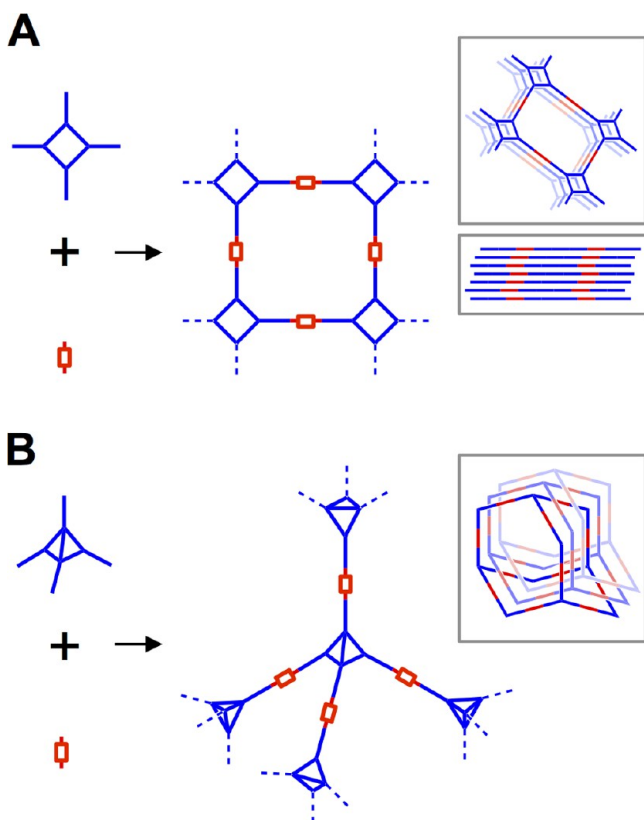


Figure 1. COF topologies are set by the symmetries of their monomers. (A) A 2D square lattice derived from square planar and linear comonomers. The insets show a prospective view (top) and side view (bottom) that depict van der Waals stacking between layers. (B) A 3D diamondoid net derived from tetrahedral and linear comonomers. The inset shows the interpenetration of congruent networks.

forming process.^{23,24} A recent example uses metal coordination approaches first developed for mechanically interlocked molecules²⁵ to access all-organic networks following demetalation.²⁶ In contrast, it remains difficult to predict how most small molecules, linear polymers, and cross-linked macromolecules arrange in the solid state.

- **Crystallinity.** COFs are ordered structures, which facilitate their design and enables characterization using diffraction techniques. Structural studies and computational tools provide predictive and powerful insight into their properties.^{27,28} This structural uniformity is also potentially attractive for catalysis, optoelectronic devices, and membranes.
- **Porosity.** The assembly of monomers into 2D and 3D networks carves out periodic, uniform voids with tailorable hydrophobicity,^{29,30} chemical affinity,^{31,32} or molecular functionality along their walls.^{33,34} Surface areas exceeding 2,500 and 4,000 m² g⁻¹ have been reported for 2D^{35,36} and 3D COFs, respectively.^{37,38}
- **Stability.** COFs are composed of robust covalent bonds. Typical frameworks are stable to temperatures exceeding 300 °C and are insoluble and impervious to solvents that do not interfere with their linkages or stacking. Recently developed COFs are highly stable to hydrolysis,^{39,40} extreme pHs,^{41,42} and reductive⁴³ and oxidative environ-

ments.⁴⁴ These materials show enhanced stability compared to most metal–organic frameworks (MOFs).

- **Low Density.** COFs are composed of lightweight elements and can potentially offer high gravimetric performance for energy and molecular storage.

In this Outlook, we will highlight leading examples that leverage the above features to construct COFs with promising properties. These examples are intended to be representative, not comprehensive, and will illustrate the exciting potential of these materials. However, several roadblocks remain to fulfill this potential, most notably in improving their average crystalline domain sizes beyond tens of nanometers and establishing powerful and convenient methods to process COFs into useful forms. We trace many of these outstanding challenges to our incomplete understanding of COF structure and formation, which also leads to poor morphological control over the final state of the material. In these areas, we highlight recent developments and opportunities for progress. The development of new COF chemistries, advancing these materials to application-relevant forms, and further structural and mechanistic understanding will establish COFs as a useful and powerful platform to connect molecular design principles to desired properties. We envision that COF formation and other syntheses conducted on surfaces and other interfaces will provide powerful control of polymerization in 2D and 3D.

EMERGING APPLICATIONS

The storage and separation of commodity and environmentally relevant gases has been a focus of both metal–organic framework (MOF) and porous polymer research for many years, and most early studies of COFs focused on these applications.⁴⁵ Although the lightweight nature of COFs is attractive in this context, many other materials systems show promise for simultaneously controlling porosity and exhibiting ideal thermodynamic adsorption parameters while minimizing cost. Many new potential applications have emerged that harness the specific placement of functional monomers and relatively large pores (2–5 nm) obtainable in 2D COF topologies.

Catalysis. Several strategies impart catalytic activity to COFs, including using monomers that function as catalysts or by postsynthetic functionalization with metal ions or organocatalysts. Chang, Yaghi, and co-workers synthesized cobalt porphyrin COFs that catalyze the electrochemical reduction of CO₂ with promising activity and selectivity over the competing process of H₂ formation (Figure 2, COF-366-Co).⁴⁶ The material exhibited a turnover number (TON) of 34,000 after 24 h, representing a 4-fold higher activity per electroactive Co relative to a molecular Co porphyrin analogue. Moreover, the material also had a 10% increase in CO:H₂ selectivity. Preliminary experiments with oriented thin films showed improved lifetimes that were attributed to reduced delamination from the electrode. In order to balance the rate of mass transport and conductivity, it will be desirable to optimize the film thickness.

COFs have shown promise as structurally precise supports for asymmetric catalysis. Cui and co-workers synthesized a tartaric acid derived imine-linked COF and later functionalized these groups using Ti(OiPr)₄ (Figure 2, CCOF-1).⁴⁷ This framework catalyzed the asymmetric addition of diethylzinc to aldehydes. For aldehydes with electron withdrawing groups, the catalyst achieved >94% conversion and >90% ee. Moreover, the

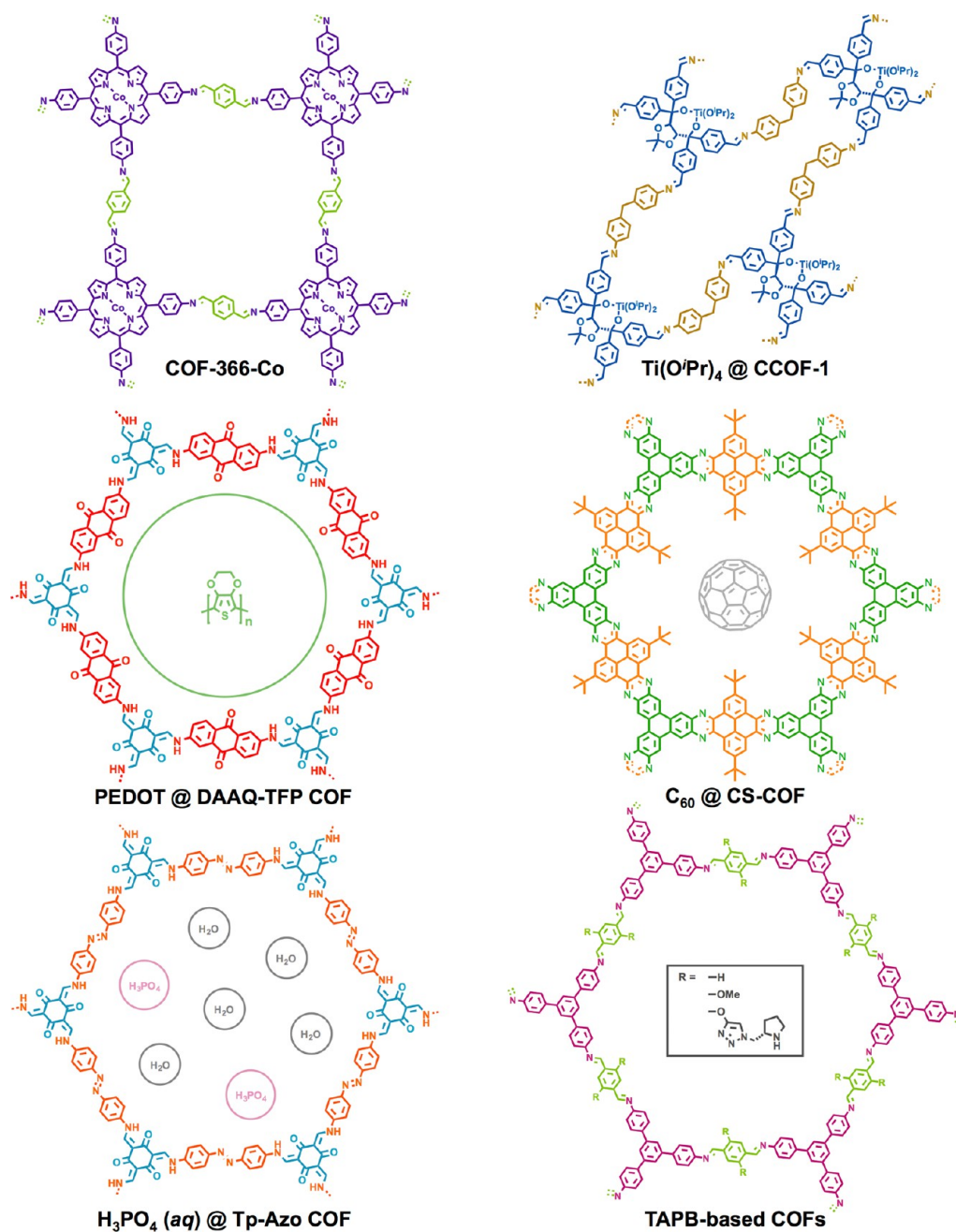


Figure 2. Structure and composition of notable COFs and their composites: imine-linked electrocatalyst COF-366-Co (top left); imine-linked tartaric acid derived catalyst CCOF-1 functionalized with $\text{Ti}(\text{O}i\text{Pr})_4$ (top right); β -ketoenamine-linked redox-active DAAQ-TFP COF containing PEDOT within its pores (middle left); phenazine-linked, hole-conductive CS-COF functionalized with C_{60} (middle right); β -ketoenamine-linked, proton-conductive Tp-Azo COF loaded with aqueous phosphoric acid (bottom left); and various derivatives of imine-linked TAPB-based COFs reported for catalysis (pyrrolidine derivative) and proton conduction ($-\text{OMe}$ derivative) when loaded with nitrogen-containing heterocycles (bottom right).

catalyst was recovered and cycled with no apparent loss in activity or selectivity. Similar behavior was observed for Michael addition reactions in an imine-linked COF with pores functionalized with (*S*)-pyrrolidine groups (Figure 2, TAPB-based COF).⁴²

One of the promises of COF-based (and other framework-based) catalysis is to combine well-defined structures with advantages of heterogeneous catalysts, which are readily reused or incorporated into continuous processes. But commonly reported catalyst recycling experiments provide only limited information when they are repeatedly run to full substrate

conversion.⁴⁸ We encourage reporting turnover numbers (TONs) and turnover frequencies (TOFs) for new COF-based catalysts to benchmark their activity and stability more rigorously.

Energy Storage. Their inherently high surface areas and ability to incorporate redox-active groups makes COFs of interest for electrochemical capacitors.^{49,50} Moreover the stability and insolubility of COFs allow for devices that perform consistently over thousands of cycles. We reported a β -ketoenamine-linked COF with anthraquinone moieties (Figure 2, DAAQ-TFP COF), which showed reversible redox

processes.⁵¹ The conductivity of the framework limited the number of redox-active quinones that could be accessed in electrodes functionalized using bulk material or oriented films.⁵² This limitation was overcome by electropolymerizing EDOT within the pores of DAAQ-TFP COF films, after which even relatively thick films ($>1 \mu\text{m}$) showed outstanding electrochemical performance.⁵³ This conductive additive increased the volumetric capacitance by accessing the previously inactive quinones and enabled charge cycling at high C-rates with minimal capacitance loss. The energy and power densities achieved in this system demonstrate that COF-based materials may soon outperform state-of-the-art carbon-based electrodes.

Membranes. Owing to their tunable pores and exceptional stability in aqueous acid, β -ketoenamine-linked COFs were investigated as proton-conductive membranes intended for fuel cells. Banerjee and co-workers synthesized an azobenzene-containing, β -ketoenamine-linked COF that was doped with phosphoric acid (Figure 2, Tp-Azo COF).⁵⁴ This COF exhibited remarkable proton conductivity near room temperature that plateaued at $9.9 \times 10^{-4} \text{ S cm}^{-1}$ at 34°C . An isostructural stilbene-containing COF showed greatly reduced performance, demonstrating the role of nitrogen atoms along the pore surfaces for proton conductivity. Similarly, Jiang and co-workers reported a triazole-functionalized imine-linked COF with conductivities of $1.1 \times 10^{-4} \text{ S cm}^{-1}$ at 130°C (Figure 2, TAPB-based COF [R = -OMe]).⁵⁵

Light Conversion. 2D COFs have been designed for light conversion because they organize functional aromatic systems into layered structures with good π -orbital overlap, which resembles proposed ordered heterojunctions.⁵⁶ One of the most promising of these systems was a phenazine-linked COF formed from the condensation of hexaaminotriphenylene and a pyrenetetrone (Figure 2, CS-COF).⁵⁷ The planarity and aromaticity of this linkage are likely responsible for the COF's impressive hole mobility of $4.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is the highest of any known COF and competitive with conventional organic semiconductors. Functionalization of this material with C_{60} and PCBM yielded a photovoltaic device with an optimized 0.9% power conversion efficiency, the current record for COF-based photovoltaics. This modest efficiency relative to the broader field of organic photovoltaics highlights the need for improved control over the materials quality, morphology, and processing. Moreover, the presumed irreversibility of the aromatization step in the synthesis of CS-COF suggests that monomer rigidity plays an important role in the formation of crystalline COFs with domain sizes in the tens of nanometers—dynamic bond formation may not be operative in all cases, even when crystallinity is observed.

■ OUTLOOK

The above emerging applications leverage the structural precision, tunable porosity, and uniformity of COFs. Yet this field is far from mature, and many fundamental advances remain for these materials to maximize their utility. Although there has been a significant expansion of COF linkage chemistries,¹³ the full scope of compatible polymerizations and pore modifications are not yet known. Perhaps more importantly, improved materials quality as judged by average crystallite size, surface area, or other application-specific metrics, control of morphology, and the improved characterization of structure and defects are all important challenges that should be addressed.

Improved Materials Quality and Characterization. The structural characterization of COFs relies on bulk techniques, which provide limited information about the uniformity, defects, and edge functionalities within the material. Most new networks are discovered by screening reaction conditions using powder X-ray diffraction (PXRD). After screening, crystalline materials are resynthesized and characterized using bulk techniques, such as infrared and solid-state NMR spectroscopies and combustion analysis. In addition to refinement of the PXRD patterns, which often exhibit a small number of reflections, porosimetry confirms the formation of a high surface area structure and estimates the pore size distribution. These techniques have so far described solvothermally grown COFs with reasonable accuracy, in agreement with calculated structures³⁹ and occasional TEM images,⁵⁸ but they have two main limitations. First, they assume uniformity of the sample, which may be qualitatively assessed by SEM, but a more rigorous quantitative assessment is lacking. Second, PXRD does not provide sufficient resolution to assess the precise conformations and relative positions of monomers within the polymeric framework, which is of particular importance for electronic applications or precise pore engineering. This need for improved structural characterization is well exemplified in the interlayer stacking of 2D COFs. Theoretical studies of the stacking of 2D COFs predict offset stacked layers rather than perfectly eclipsed average structure derived from powder refinement.^{59–61} These offsets form one or more nearly degenerate stacking topologies based on three layers (Figure 3).⁶² The offset direction is unlikely to be monotonic through the layered structure and is instead distributed among the various possible directions or even within 2D grains of the same layer. This aspect of COF structure has not been confirmed experimentally, but it is expected to influence the electronic coupling between layers and the effective pore size by as much as 0.5 nm. Other major structural questions remain largely unexplored, such as assessing the percent crystallinity of the material, the occurrence and nature of defects such as vacancies and inclusions, the size distribution and relative orientations of crystalline domains, and the atomic structures of grain boundaries.

Addressing these outstanding structural questions is not easy. Difficulties arise primarily from the polycrystallinity and relatively small domain sizes of solvothermally synthesized COFs. Moreover, methods that probe these questions at the nanoscale, such as TEM, are more easily applied to materials composed of heavier elements. Unlike MOFs, single crystal structures are not readily obtained and are limited to a few examples. A notable exception reported by Wuest and co-workers involved the synthesis of microscopic crystals of 3D COFs based on the reversible dimerization of polyfunctional nitroso compounds (Figure 4A).⁶³ Uniform single crystals of the 3D COFs were obtained with diameters on the order of tens of micrometers, but this finding has not yet been generalized to 2D networks or other linkage chemistries. Yaghi and co-workers performed rotation electron diffraction on a nanometer-sized 3D COF crystal via TEM (Figure 4B). Using this method the crystal structure of a 3D imine-linked COF was solved at 89 K from a bulk polycrystalline sample.⁶⁴ Techniques under development for the study of biomacromolecules or other 2D materials might also prove suitable for the study of COFs. Cryo-electron microscopy has enabled reconstruction of even low kDa structures with resolutions nearing 2 Å.⁶⁵ Encapsulation has been used to stabilize or

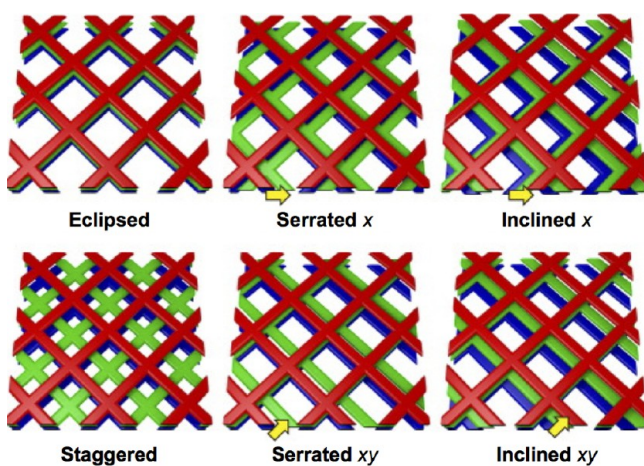


Figure 3. Various interlayer stacking modes possible for 2D square lattice COFs when considering a 3-layer system. Adapted with permission from ref 62. Copyright 2016 Elsevier.

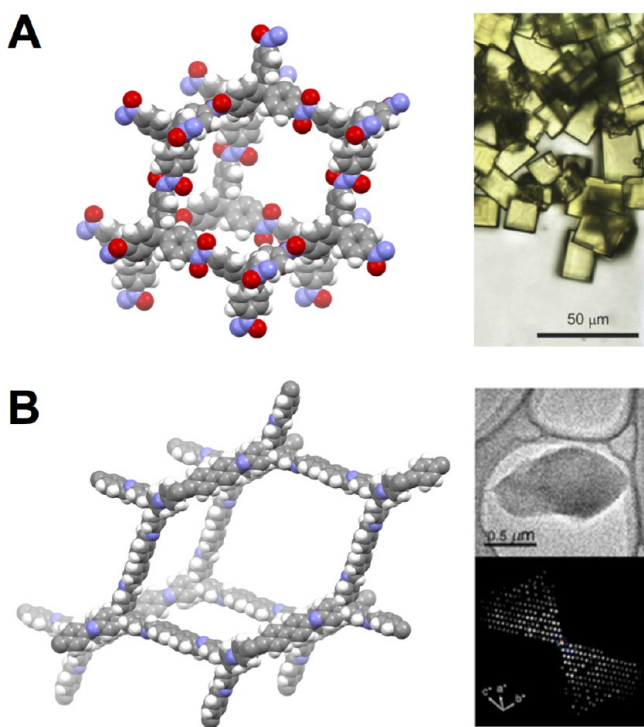


Figure 4. Solved 3D COF crystal structures. (A) The structure of an azodioxy-linked COF (left) solved from macroscopic single crystals (right). Adapted with permission from ref 63. Copyright 2013 Nature Publishing Group (NPG). (B) The structure of an imine-linked COF (left) solved by rotational electron diffraction of the crystallite (right) for which a representative diffraction pattern for a single rotation is shown. Adapted with permission from ref 64. Copyright 2013 American Chemical Society (ACS).

reduce radiation damage of single-layer 2D inorganic materials such as MoS_2 ⁶⁶ and gallium nitride.⁶⁷ Likewise, nanoscale optical characterization of COFs represents a new opportunity to characterize uniformity and defects in COFs.⁶⁸ As the field continues to elaborate COFs into composite materials, the need for improved characterization will be essential to understand and improve their performance.

Increasing the average crystallite size and obtaining single crystals of many COFs is therefore one of the most important

challenges to the field. Toward this end, we believe that current practice of screening polymerizations by PXRD is predisposed to identifying conditions for which nucleation is uncontrolled and precipitation happens quickly, resulting in small crystalline domains. Very little is known about the appropriate polymerization or requisite error correction rates that will give rise to improved materials quality. This deficiency stands in contrast to the more mature field of controlled radical polymerization, in which the rates that govern chain growth and deactivation processes are carefully balanced to provide well-defined polymers from irreversible reactions.^{69,70} This inspired our ongoing mechanistic studies of COF formation where we first explored the rate of precipitation of 2D boronate ester-linked COFs by measuring the solution turbidity as a function of reaction time from an initially homogeneous monomer solution (Figure 5A).^{71,72} These conditions provide reproducible induction periods during which soluble oligomers form and nucleation occurs. After a few minutes at 90 °C, the crystalline COF begins to precipitate (Figure 5B). The turbidity of this solution tracks the rate of COF precipitation (Figure 5C). A monofunctional catechol competitor added either initially or during COF polymerization slowed the rate of formation comparably, suggesting reversibility in the early stages of COF growth, but did not increase the average crystallite size (Figure 5D). When adding the competitor in excess, precipitated COF material did not revert to soluble species, suggesting irreversibility in the later stages of COF formation (Figure 6, top). In contrast, the addition of water, which does hydrolyze precipitated COF, doubled the average crystallite domain size. Bein and co-workers observed similar improvements in average domain size using monofunctional boronic acid additives.⁷³ COFs formed in the presence of this competitor showed greatly increased domain sizes, the largest of which were observed to be hundreds of nanometers, and surface areas that approached theoretical values. Furthermore, the monofunctional boronate ester competitor resides primarily at the surface of COF crystallites rather than a defect in the bulk framework and was used to functionalize the outer surfaces. For imine-linked COFs, we observed a different growth mechanism than with the boronate ester system. Polyfunctional amine and aldehyde monomers rapidly condense to form amorphous imine-linked polymer networks, which rearrange into 2D layered structures (Figure 6, bottom).⁷⁴ Although this restructuring typically occurs under the reaction conditions, it is also possible to isolate the amorphous polymer and convert it to a 2D COF by resubjecting it to water and acid in the absence of additional monomers.

Another strategy to improve COF crystallinity has been to design monomers that are predisposed to form ordered structures. Bein and co-workers employed monomers with screw or propeller-like shapes, which stack in a single, distinct way (Figure 7A).^{75,76} This design eliminates the degenerate offsets thought to be present in other 2D COFs (Figure 3, Figure 7C), potentially facilitating fusion across grain boundaries (Figure 7B). Jiang and co-workers achieved similarly improved crystallinity by tuning the π -electron interactions of the monomers.⁷⁷ They showed that using a mixture of terephthalaldehyde and its perfluorinated analogue increased the interlayer stacking energy and resulted in 2D imine-linked COFs with improved crystallinity and surface area relative to the structures composed of either monomer alone. They separately demonstrated that stacking energy and crystallinity could be similarly increased by minimizing

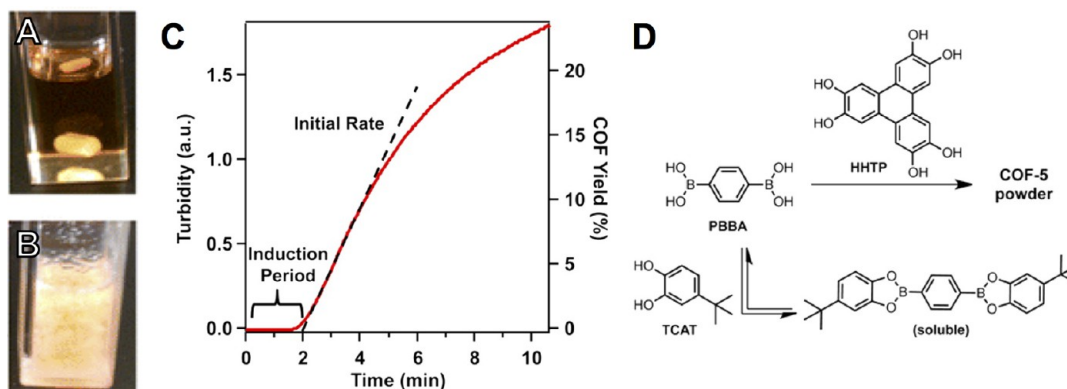


Figure 5. Mechanistic study of COF-5 synthesis where initially homogeneous solution (A) becomes turbid as COF-5 precipitates (B). (C) Turbidity measurements of COF formation in which, following an induction period, an initial rate is measured. (D) Reaction scheme for COF-5 formation in the presence of a catechol competitor. Adapted with permission from ref 71. Copyright 2014 ACS.

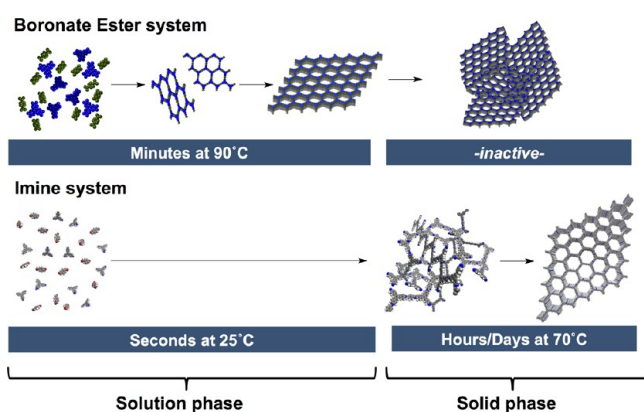


Figure 6. Contrasting mechanisms proposed for the crystallization of boronate ester-linked (top) and imine-linked (bottom) COFs.

interlayer charge repulsion.⁴² The electron-withdrawing nature of the imine linkages provides for electropositive π -systems that stack less favorably compared to an electroneutral system. For example, a terephthalaldehyde-containing COF (Figure 2, TAPB-based COF [R = H]) exhibited only modest crystallinity and a surface area of $6 \text{ m}^2 \text{ g}^{-1}$, yet dimethoxyterephthalaldehyde with π -electron-donating groups provided enhanced crystallinity from identical polymerization conditions (R = -OMe). Furthermore, the dimethoxyterephthalaldehyde-based COF exhibited a surface area $>2,000 \text{ m}^2 \text{ g}^{-1}$, which is among the highest reported for 2D COFs. These monomer designs based on secondary geometric features or electronic effects offer improved materials quality and insight into COF formation; however, they limit the monomer generality. While demonstrably successful, it is important to note that COFs lacking these design criteria have since been prepared with similarly high surface areas. For example the terephthalaldehyde-containing COF (R = H) was prepared with a surface area of $600 \text{ m}^2 \text{ g}^{-1}$ by optimizing the water and acetic acid concentrations.⁷⁴ Additionally, $\text{Sc}(\text{OTf})_3$, a water-tolerant Lewis acid catalyst, provides samples of the same COF with surface areas $>2,000 \text{ m}^2 \text{ g}^{-1}$ in only 10 min at room temperature.⁷⁸ These findings caution against general conclusions regarding monomer design without broadly exploring optimal polymerization and activation protocols.

Improved Morphological Control. Many promising properties are measured and potential applications inferred from COFs prepared as microcrystalline powders, but fulfilling

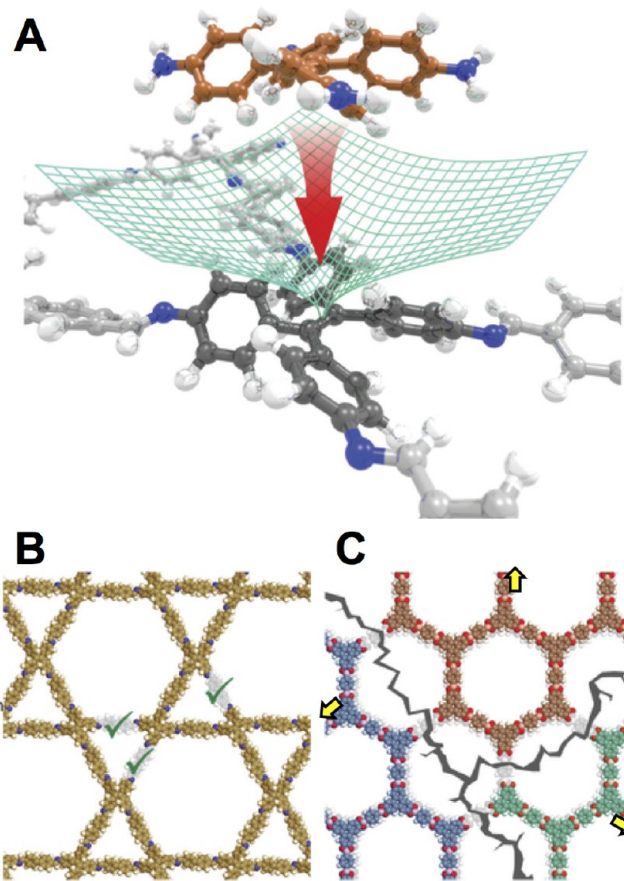


Figure 7. A geometric monomer design strategy to facilitate COF crystallization. (A) The stacking of a propeller shaped monomer on a 2D COF layer and the steep, singular-welled potential energy surface that necessitates its eclipsed stacking. (B) Docking sites for fusing together of neighboring island domains nucleated on a layer of COF using this strategy. (C) Similar sites in 2D COFs may be left as vacancies or result in strain upon fusion due to incongruent interlayer stacking offsets as indicated by the yellow arrows. Adapted with permission from ref 75. Copyright 2016 NPG.

this promise will require improved control over the morphology and isolated form of the polymer. For example, Uribe-Romo and co-workers demonstrated promising Li-ion conduction in pressed pellets of 2D COFs which showed preferred crystallite orientation as a result of the pressing

process.⁷⁹ COF powders have also been shoehorned into devices that measure their photoconductivity and photovoltaic performance,⁸⁰ redox activity, and proton or ionic conductivity, among other properties. However, improved performance and relevance for applications that leverage these properties require robust methods to form thin films, freestanding membranes, or other functional forms.

There are now several available methods to grow 2D COFs as thin films on arbitrary substrates. The simplest method is to include the desired film substrate in the solvothermal synthesis conditions (Figure 8A). We prepared oriented, 2D COF thin films on single-layer graphene and other substrates and showed that their stacking direction was normal to the substrate using grazing incidence X-ray diffraction.⁸¹ Subsequently, Bein and co-workers showed that similar films can be grown on transparent conducting substrates, such as ITO, and have measured their anisotropic charge transport properties in addition to preparing photoelectric devices.^{82,83} COF thin films grown in this way have also shown promise as electrocatalysts and energy storage devices. This method of film growth, though simple, does not provide effective control over either the film location or thickness. Moreover, the film surface becomes contaminated with COF powders that precipitate simultaneously. One solution is to identify conditions in which film growth occurs selectively. We found conditions under which a Zn phthalocyanine based boronate ester COF formed exclusively on single layer graphene, yet thickness control was still difficult in this system.⁸⁴ The top-down patterning of COF films was also recently reported by Lu and co-workers.⁸⁵ Alternatively, we demonstrated the growth of

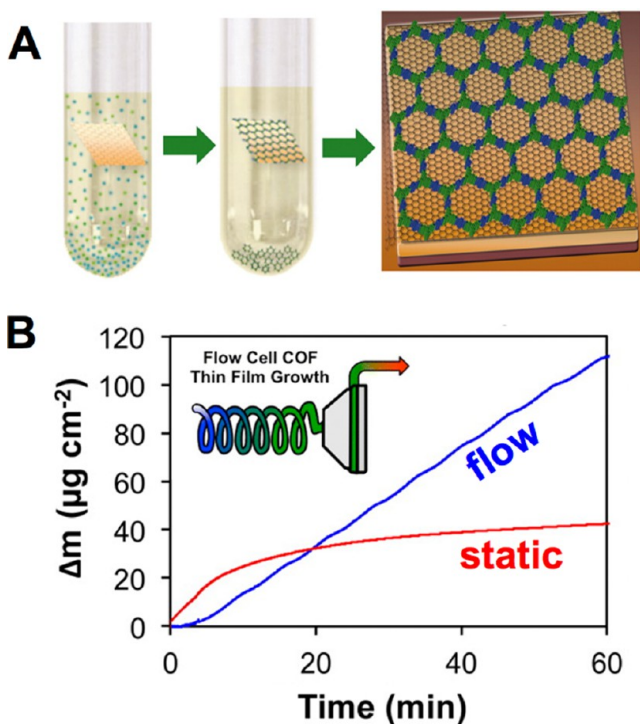


Figure 8. Oriented thin film formation of 2D COFs. (A) The solvothermal growth of 2D boronate ester-linked COFs on single layer graphene. Adapted with permission from ref 81. Copyright 2011 AAAS. (B) Change in Sauerbrey mass as boronate ester-linked COF thin film-grown either solvothermally (red) or from heated flow (blue). Adapted with permission from ref 86. Copyright 2016 ACS.

boronate ester-linked 2D COF thin films from a flowed solution that afforded control of the deposition rate, film thickness, and crystallinity (Figure 8B).⁸⁶ As bulk powder formed downstream of the film substrate, we also synthesized films with reduced roughness preferable for electronic applications such as field effect transistors.⁸⁷ It should be noted, however, that this methodology is highly wasteful of monomer in the absence of a process to isolate or reuse monomers from the outflow.

Colloidal COFs are another attractive morphology as they are potentially compatible with solution processing techniques. Banerjee and co-workers reported hollow core-shell COF structures capable of protein immobilization that could therefore be used as a biosensor or biocatalyst.⁸⁸ We recently reported the synthesis of boronate ester-linked COFs as stable colloids (Figure 9A).⁸⁹ The size of the colloids is controllable with narrow dispersity without sacrificing crystallinity. This suspension may be amenable to traditional solution processing techniques as a free-standing film was obtained upon solvent evaporation. Besides direct synthesis, COF colloids can also be formed on a template to make hybrid core-shell structures, as demonstrated by Guo and co-workers, who formed COF-coated Fe_3O_4 nanoparticles (Figure 9B,C) enabling them to be manipulated by magnetic fields (Figure 9D).⁹⁰

The synthesis of 2D COFs as a few-layer or monolayer structure is also desirable as unique materials properties may emerge at the single- to few-layer limit. As with other 2D

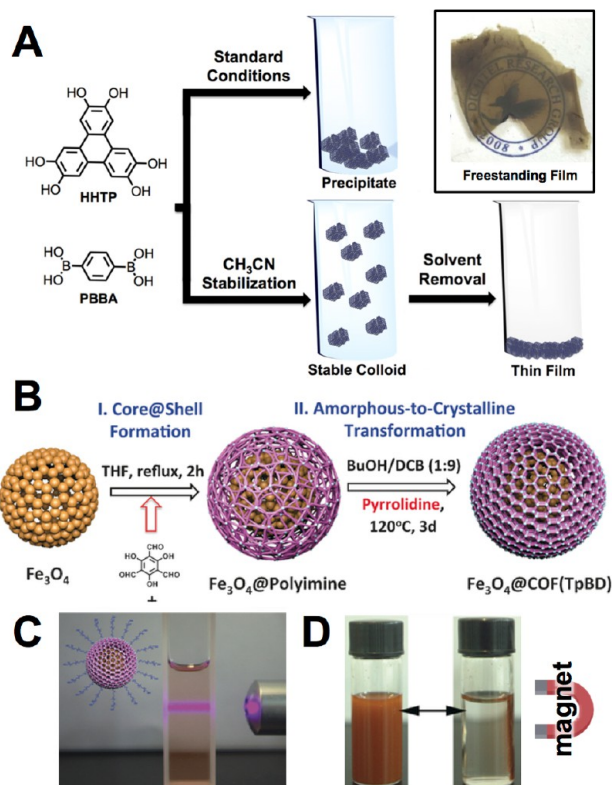


Figure 9. Colloidal COF systems. (A) Boronate ester-linked COFs form as colloids in the presence of nitrile cosolvents and were processed into free-standing films (inset). Adapted with permission from ref 89. Copyright 2017 ACS. (B) The formation of an imine COF shell on an Fe_3O_4 nanoparticle and demonstrations of the hybrid's Tyndall effect and magnetism (C, D). Adapted with permission from ref 90. Copyright 2016 John Wiley & Sons, Inc.

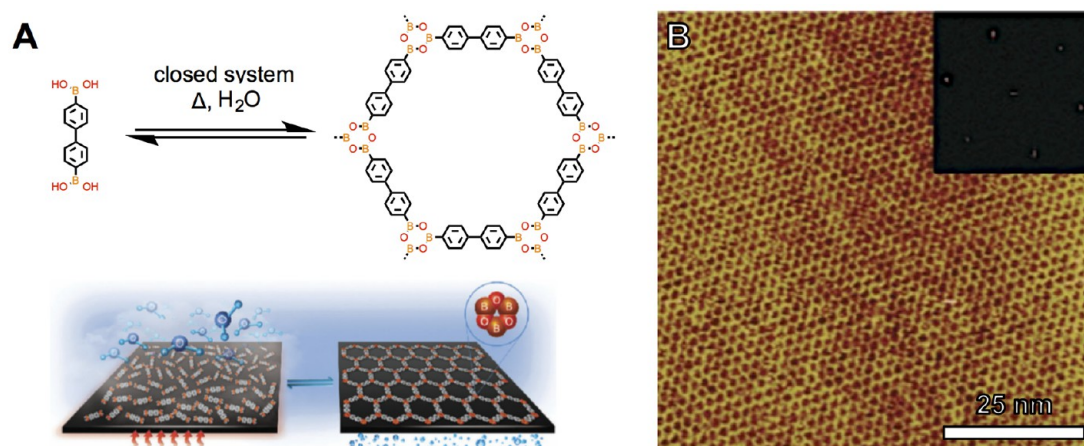


Figure 10. (A) Formation of a boroxine-linked COF as a monolayer when confined to a surface and annealed in the presence of H₂O to yield large crystalline domains. (B) STM image of a BPDA COF monolayer grown by this method. (Inset is the Fourier transform of the STM image.) Adapted with permission from ref 107. Copyright 2011 The Royal Society of Chemistry.

materials,⁹¹ exfoliation has proven to be a viable strategy to these atomically thin structures.^{92–94} Little emphasis has been placed on optimizing yield or uniformity from the exfoliation process or developing methodologies to enrich or purify the number of layers or lateral size exfoliated supernatant.⁹⁵ Moreover, confirmation of a crystalline structure for these nanoscopic flakes is nontrivial. That being said, exfoliated suspensions offer a novel avenue toward processable COFs.^{96,97} The Zhao and Banerjee groups both demonstrated the use of exfoliated COFs in composite membranes for CO₂ separation and biomedical applications, respectively.^{98–100}

A separate strategy has been the direct growth of monolayers on substrates typically by UHV methods. In this unique case, direct resolution of crystallite domains and their defects are possible by STM for conductive substrates. Moreover, these systems enable reaction chemistries for which crystallization conditions of the analogous solvothermally grown COFs are unknown and potentially unobtainable such as by Ullman coupling^{101–104} or polyester condensation.¹⁰⁵ Obtaining high surface coverage and good long-range order has been difficult by this methodology and has been the primary focus of work thus far. For instance, solvent annealing by introducing water at elevated temperatures has afforded large area surface confined COFs of both boroxine^{106,107} and imine-linked frameworks (Figure 10).^{108,109} Likewise reducing monomer concentration was found to bias the formation of large area single-layer boronate ester frameworks at room temperature.¹¹⁰ Thus far, measuring the properties of these monolayers or their incorporation functional devices has not been achieved. One notable exception was demonstrated by Lei and co-workers, who formed a photoresponsive, surface-confined COF capable of capture and release of a phthalocyanine guest molecule.¹¹¹

A third strategy to emerge recently is the growth of COFs at the air–water interface. Zhang and co-workers demonstrated that monolayer films could be obtained and subsequently transferred to arbitrary substrates.¹¹² Subsequently, Feng and co-workers demonstrated the ability to make wafer-sized films by this technique and further characterized their mechanical robustness and performance as the active semiconducting layer in a transistor device.¹¹³ Although these reports do not demonstrate crystallinity of these monolayers, this strategy could prove useful for the synthesis of large-area, free-standing 2D polymers.

CONCLUSION

The primary focus of the COF field has been to expand linkage chemistries and topologies and to identify properties of applied interest. These directions remain important and fertile ground. Yet perhaps even larger hurdles remain in characterizing COFs and improving their materials quality; understanding the mechanisms and optimal crystallization conditions; and developing methods to process COFs into devices, free-standing films, and other useful forms. Progress will enable the rational design of heterogeneous, single-site catalysts; energy storage and generation systems; and membranes with tunable pore size, shape, and functionality. The modularity afforded by COF design strategies justifies heavy investments in these more fundamental questions. With improved mechanism-guided syntheses and morphological control, the fundamental and even commercial success of COF materials and/or synthetic 2D polymers may soon be realized.

AUTHOR INFORMATION

Corresponding Author

*E-mail: wlichtel@northwestern.edu.

ORCID

Ryan P. Bisbey: 0000-0001-8699-5077

William R. Dichtel: 0000-0002-3635-6119

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the United States Army Research Office for a Multidisciplinary University Research Initiative (MURI) award under Grant No. W911NF-15-1-0447. W.R.D. was also supported by the Camille and Henry Dreyfus Foundation through a Camille Dreyfus Teacher-Scholar Award.

REFERENCES

- (1) Hawker, C. J.; Wooley, K. L. The Convergence of Synthetic Organic and Polymer Chemistries. *Science* **2005**, *309*, 1200–1205.
- (2) Stupp, S. I.; Palmer, L. C. Supramolecular Chemistry and Self-Assembly in Organic Materials Design. *Chem. Mater.* **2014**, *26*, 507–518.

- (3) Badjić, J. D.; Nelson, A.; Cantrill, S. J.; Turnbull, W. B.; Stoddart, J. F. Multivalency and Cooperativity in Supramolecular Chemistry. *Acc. Chem. Res.* **2005**, *38*, 723–732.
- (4) Zhou, H.-C.; Kitagawa, S. Metal–Organic Frameworks (MOFs). *Chem. Soc. Rev.* **2014**, *43*, 5415–5418.
- (5) Chen, L.; Chen, Q.; Wu, M.; Jiang, F.; Hong, M. Controllable Coordination-Driven Self-Assembly: From Discrete Metallocages to Infinite Cage-Based Frameworks. *Acc. Chem. Res.* **2015**, *48*, 201–210.
- (6) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. Dynamic Covalent Chemistry. *Angew. Chem., Int. Ed.* **2002**, *41*, 898–952.
- (7) Jin, Y.; Yu, C.; Denman, R. J.; Zhang, W. Recent Advances in Dynamic Covalent Chemistry. *Chem. Soc. Rev.* **2013**, *42*, 6634–6654.
- (8) Biradha, K.; Santra, R. Crystal Engineering of Topochemical Solid State Reactions. *Chem. Soc. Rev.* **2013**, *42*, 950–967.
- (9) Richman, E. K.; Hutchison, J. E. The Nanomaterial Characterization Bottleneck. *ACS Nano* **2009**, *3*, 2441–2446.
- (10) Diercks, C. S.; Yaghi, O. M. The Atom, the Molecule, and the Covalent Organic Framework. *Science* **2017**, *355*, eaal1585.
- (11) Huang, N.; Wang, P.; Jiang, D. Covalent Organic Frameworks: A Materials Platform for Structural and Functional Designs. *Nat. Rev. Mater.* **2016**, *1*, 16068.
- (12) Waller, P. J.; Gándara, F.; Yaghi, O. M. Chemistry of Covalent Organic Frameworks. *Acc. Chem. Res.* **2015**, *48*, 3053–3063.
- (13) DeBlase, C. R.; Dichtel, W. R. Moving Beyond Boron: The Emergence of New Linkage Chemistries in Covalent Organic Frameworks. *Macromolecules* **2016**, *49*, 5297–5305.
- (14) Dogru, M.; Bein, T. On the Road towards Electroactive Covalent Organic Frameworks. *Chem. Commun.* **2014**, *50*, 5531–5546.
- (15) Wuest, J. D. Engineering Crystals by the Strategy of Molecular Tectonics. *Chem. Commun.* **2005**, *0*, 5830–5837.
- (16) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. Supramolecular Coordination: Self-Assembly of Finite Two- and Three-Dimensional Ensembles. *Chem. Rev.* **2011**, *111*, 6810–6918.
- (17) Yoshizawa, M.; Klosterman, J. K.; Fujita, M. Functional Molecular Flasks: New Properties and Reactions within Discrete, Self-Assembled Hosts. *Angew. Chem., Int. Ed.* **2009**, *48*, 3418–3438.
- (18) Robson, R. Net-Based Approach to Coordination Polymers. *J. Chem. Soc., Dalton Trans.* **2000**, 3735–3744.
- (19) Spitler, E. L.; Colson, J. W.; Uribe-Romo, F. J.; Woll, A. R.; Giovino, M. R.; Saldivar, A.; Dichtel, W. R. Lattice Expansion of Highly Oriented 2D Phthalocyanine Covalent Organic Framework Films. *Angew. Chem., Int. Ed.* **2012**, *51*, 2623–2627.
- (20) Yang, H.; Du, Y.; Wan, S.; Trahan, G. D.; Jin, Y.; Zhang, W. Mesoporous 2D Covalent Organic Frameworks Based on Shape-Persistent Arylene-Ethynylene Macrocycles. *Chem. Sci.* **2015**, *6*, 4049–4053.
- (21) Zhu, Y.; Wan, S.; Jin, Y.; Zhang, W. Desymmetrized Vertex Design for the Synthesis of Covalent Organic Frameworks with Periodically Heterogeneous Pore Structures. *J. Am. Chem. Soc.* **2015**, *137*, 13772–13775.
- (22) Huang, N.; Zhai, L.; Couprie, D. E.; Addicoat, M. A.; Okushita, K.; Nishimura, K.; Heine, T.; Jiang, D. Multiple-Component Covalent Organic Frameworks. *Nat. Commun.* **2016**, *7*, 12325.
- (23) Chen, X.; Addicoat, M.; Jin, E.; Xu, H.; Hayashi, T.; Xu, F.; Huang, N.; Irle, S.; Jiang, D. Designed Synthesis of Double-Stage Two-Dimensional Covalent Organic Frameworks. *Sci. Rep.* **2015**, *5*, 14650.
- (24) Yue, J.-Y.; Mo, Y.-P.; Li, S.-Y.; Dong, W.-L.; Chen, T.; Wang, D. Simultaneous Construction of Two Linkages for the on-Surface Synthesis of Imine–boroxine Hybrid Covalent Organic Frameworks. *Chem. Sci.* **2017**, *8*, 2169–2174.
- (25) Chichak, K. S.; Cantrill, S. J.; Pease, A. R.; Chiu, S.-H.; Cave, G. W. V.; Atwood, J. L.; Stoddart, J. F. Molecular Borromean Rings. *Science* **2004**, *304*, 1308–1312.
- (26) Liu, Y.; Ma, Y.; Zhao, Y.; Sun, X.; Gándara, F.; Furukawa, H.; Liu, Z.; Zhu, H.; Zhu, C.; Suenaga, K.; Oleynikov, P.; Alshammari, A. S.; Zhang, X.; Terasaki, O.; Yaghi, O. M. Weaving of Organic Threads into a Crystalline Covalent Organic Framework. *Science* **2016**, *351*, 365–369.
- (27) Amirjalayer, S.; Snurr, R. Q.; Schmid, R. Prediction of Structure and Properties of Boron-Based Covalent Organic Frameworks by a First-Principles Derived Force Field. *J. Phys. Chem. C* **2012**, *116*, 4921–4929.
- (28) Vyas, V. S.; Haase, F.; Stegbauer, L.; Savasci, G.; Podjaski, F.; Ochsenfeld, C.; Lotsch, B. V. A Tunable Azine Covalent Organic Framework Platform for Visible Light-Induced Hydrogen Generation. *Nat. Commun.* **2015**, *6*, 8508.
- (29) Lanni, L. M.; Tilford, R. W.; Bharathy, M.; Lavigne, J. J. Enhanced Hydrolytic Stability of Self-Assembling Alkylated Two-Dimensional Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2011**, *133*, 13975–13983.
- (30) Biswal, B. P.; Kandambeth, S.; Chandra, S.; Shinde, D. B.; Bera, S.; Karak, S.; Garai, B.; Kharul, U. K.; Banerjee, R. Pore Surface Engineering in Porous, Chemically Stable Covalent Organic Frameworks for Water Adsorption. *J. Mater. Chem. A* **2015**, *3*, 23664–23669.
- (31) Ding, S.-Y.; Dong, M.; Wang, Y.-W.; Chen, Y.-T.; Wang, H.-Z.; Su, C.-Y.; Wang, W. Thioether-Based Fluorescent Covalent Organic Framework for Selective Detection and Facile Removal of Mercury(II). *J. Am. Chem. Soc.* **2016**, *138*, 3031–3037.
- (32) Huang, N.; Krishna, R.; Jiang, D. Tailor-Made Pore Surface Engineering in Covalent Organic Frameworks: Systematic Functionalization for Performance Screening. *J. Am. Chem. Soc.* **2015**, *137*, 7079–7082.
- (33) Nagai, A.; Guo, Z.; Feng, X.; Jin, S.; Chen, X.; Ding, X.; Jiang, D. Pore Surface Engineering in Covalent Organic Frameworks. *Nat. Commun.* **2011**, *2*, 536.
- (34) Xu, F.; Xu, H.; Chen, X.; Wu, D.; Wu, Y.; Liu, H.; Gu, C.; Fu, R.; Jiang, D. Radical Covalent Organic Frameworks: A General Strategy to Immobilize Open-Accessible Polyradicals for High-Performance Capacitive Energy Storage. *Angew. Chem., Int. Ed.* **2015**, *54*, 6814–6818.
- (35) Jin, S.; Furukawa, K.; Addicoat, M.; Chen, L.; Takahashi, S.; Irle, S.; Nakamura, T.; Jiang, D. Large Pore Donor–acceptor Covalent Organic Frameworks. *Chem. Sci.* **2013**, *4*, 4505–4511.
- (36) Rabbani, M. G.; Sekizkardes, A. K.; Kahveci, Z.; Reich, T. E.; Ding, R.; El-Kaderi, H. M. A 2D Mesoporous Imine-Linked Covalent Organic Framework for High Pressure Gas Storage Applications. *Chem. - Eur. J.* **2013**, *19*, 3324–3328.
- (37) El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortés, J. L.; Côté, A. P.; Taylor, R. E.; O’Keeffe, M.; Yaghi, O. M. Designed Synthesis of 3D Covalent Organic Frameworks. *Science* **2007**, *316*, 268–272.
- (38) Baldwin, L. A.; Crowe, J. W.; Pyles, D. A.; McGrier, P. L. Metalation of a Mesoporous Three-Dimensional Covalent Organic Framework. *J. Am. Chem. Soc.* **2016**, *138*, 15134–15137.
- (39) Uribe-Romo, F. J.; Doonan, C. J.; Furukawa, H.; Oisaki, K.; Yaghi, O. M. Crystalline Covalent Organic Frameworks with Hydrazone Linkages. *J. Am. Chem. Soc.* **2011**, *133*, 11478–11481.
- (40) Du, Y.; Yang, H.; Whiteley, J. M.; Wan, S.; Jin, Y.; Lee, S.-H.; Zhang, W. Ionic Covalent Organic Frameworks with Spiroborate Linkage. *Angew. Chem., Int. Ed.* **2016**, *55*, 1737–1741.
- (41) Kandambeth, S.; Mallick, A.; Lukose, B.; Mane, M. V.; Heine, T.; Banerjee, R. Construction of Crystalline 2D Covalent Organic Frameworks with Remarkable Chemical (Acid/Base) Stability via a Combined Reversible and Irreversible Route. *J. Am. Chem. Soc.* **2012**, *134*, 19524–19527.
- (42) Xu, H.; Gao, J.; Jiang, D. Stable, Crystalline, Porous, Covalent Organic Frameworks as a Platform for Chiral Organocatalysts. *Nat. Chem.* **2015**, *7*, 905–912.
- (43) Lohse, M. S.; Stassin, T.; Naudin, G.; Wuttke, S.; Ameloot, R.; De Vos, D.; Medina, D. D.; Bein, T. Sequential Pore Wall Modification in a Covalent Organic Framework for Application in Lactic Acid Adsorption. *Chem. Mater.* **2016**, *28*, 626–631.
- (44) Waller, P. J.; Lyle, S. J.; Osborn Popp, T. M.; Diercks, C. S.; Reimer, J. A.; Yaghi, O. M. Chemical Conversion of Linkages in Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2016**, *138*, 15519–15522.
- (45) Zeng, Y.; Zou, R.; Zhao, Y. Covalent Organic Frameworks for CO₂ Capture. *Adv. Mater.* **2016**, *28*, 2855–2873.

- (46) Lin, S.; Diercks, C. S.; Zhang, Y.-B.; Kornienko, N.; Nichols, E. M.; Zhao, Y.; Paris, A. R.; Kim, D.; Yang, P.; Yaghi, O. M.; Chang, C. J. Covalent Organic Frameworks Comprising Cobalt Porphyrins for Catalytic CO₂ Reduction in Water. *Science* **2015**, *349*, 1208–1213.
- (47) Wang, X.; Han, X.; Zhang, J.; Wu, X.; Liu, Y.; Cui, Y. Homochiral 2D Porous Covalent Organic Frameworks for Heterogeneous Asymmetric Catalysis. *J. Am. Chem. Soc.* **2016**, *138*, 12332–12335.
- (48) Jones, C. W. On the Stability and Recyclability of Supported Metal–Ligand Complex Catalysts: Myths, Misconceptions and Critical Research Needs. *Top. Catal.* **2010**, *53*, 942–952.
- (49) Khattak, A. M.; Ghazi, Z. A.; Liang, B.; Khan, N. A.; Iqbal, A.; Li, L.; Tang, Z. A Redox-Active 2D Covalent Organic Framework with Pyridine Moieties Capable of Faradaic Energy Storage. *J. Mater. Chem. A* **2016**, *4*, 16312–16317.
- (50) Chandra, S.; Roy Chowdhury, D.; Addicoat, M.; Heine, T.; Paul, A.; Banerjee, R. Molecular Level Control of the Capacitance of Two-Dimensional Covalent Organic Frameworks: Role of Hydrogen Bonding in Energy Storage Materials. *Chem. Mater.* **2017**, *29*, 2074–2080.
- (51) DeBlase, C. R.; Silberstein, K. E.; Truong, T.-T.; Abruña, H. D.; Dichtel, W. R. β -Ketoenamine-Linked Covalent Organic Frameworks Capable of Pseudocapacitive Energy Storage. *J. Am. Chem. Soc.* **2013**, *135*, 16821–16824.
- (52) DeBlase, C. R.; Hernández-Burgos, K.; Silberstein, K. E.; Rodríguez-Calero, G. G.; Bisbey, R. P.; Abruña, H. D.; Dichtel, W. R. Rapid and Efficient Redox Processes within 2D Covalent Organic Framework Thin Films. *ACS Nano* **2015**, *9*, 3178–3183.
- (53) Mulzer, C. R.; Shen, L.; Bisbey, R. P.; McKone, J. R.; Zhang, N.; Abruña, H. D.; Dichtel, W. R. Superior Charge Storage and Power Density of a Conducting Polymer-Modified Covalent Organic Framework. *ACS Cent. Sci.* **2016**, *2*, 667–673.
- (54) Chandra, S.; Kundu, T.; Kandambeth, S.; BabaRao, R.; Marathe, Y.; Kunjir, S. M.; Banerjee, R. Phosphoric Acid Loaded Azo (–N=N–) Based Covalent Organic Framework for Proton Conduction. *J. Am. Chem. Soc.* **2014**, *136*, 6570–6573.
- (55) Xu, H.; Tao, S.; Jiang, D. Proton Conduction in Crystalline and Porous Covalent Organic Frameworks. *Nat. Mater.* **2016**, *15*, 722–726.
- (56) Chen, L.; Furukawa, K.; Gao, J.; Nagai, A.; Nakamura, T.; Dong, Y.; Jiang, D. Photoelectric Covalent Organic Frameworks: Converting Open Lattices into Ordered Donor–Acceptor Heterojunctions. *J. Am. Chem. Soc.* **2014**, *136*, 9806–9809.
- (57) Guo, J.; Xu, Y.; Jin, S.; Chen, L.; Kaji, T.; Honsho, Y.; Addicoat, M. A.; Kim, J.; Saeki, A.; Ihee, H.; Seki, S.; Irle, S.; Hiramoto, M.; Gao, J.; Jiang, D. Conjugated Organic Framework with Three-Dimensionally Ordered Stable Structure and Delocalized π Clouds. *Nat. Commun.* **2013**, *4*, 2736.
- (58) Wan, S.; Guo, J.; Kim, J.; Ihee, H.; Jiang, D. A Belt-Shaped, Blue Luminescent, and Semiconducting Covalent Organic Framework. *Angew. Chem., Int. Ed.* **2008**, *47*, 8826–8830.
- (59) Spitler, E. L.; Koo, B. T.; Novotney, J. L.; Colson, J. W.; Uribe-Romo, F. J.; Gutierrez, G. D.; Clancy, P.; Dichtel, W. R. A 2D Covalent Organic Framework with 4.7-Nm Pores and Insight into Its Interlayer Stacking. *J. Am. Chem. Soc.* **2011**, *133*, 19416–19421.
- (60) Lukose, B.; Kuc, A.; Heine, T. The Structure of Layered Covalent-Organic Frameworks. *Chem. - Eur. J.* **2011**, *17*, 2388–2392.
- (61) Koo, B. T.; Dichtel, W. R.; Clancy, P. A Classification Scheme for the Stacking of Two-Dimensional Boronate Ester-Linked Covalent Organic Frameworks. *J. Mater. Chem.* **2012**, *22*, 17460–17469.
- (62) Hayashi, T.; Hijikata, Y.; Page, A.; Jiang, D.; Irle, S. Theoretical Analysis of Structural Diversity of Covalent Organic Framework: Stacking Isomer Structures Thermodynamics and Kinetics. *Chem. Phys. Lett.* **2016**, *664*, 101–107.
- (63) Beaudoin, D.; Maris, T.; Wuest, J. D. Constructing Monocrystalline Covalent Organic Networks by Polymerization. *Nat. Chem.* **2013**, *5*, 830–834.
- (64) Zhang, Y.-B.; Su, J.; Furukawa, H.; Yun, Y.; Gándara, F.; Duong, A.; Zou, X.; Yaghi, O. M. Single-Crystal Structure of a Covalent Organic Framework. *J. Am. Chem. Soc.* **2013**, *135*, 16336–16339.
- (65) Merk, A.; Bartesaghi, A.; Banerjee, S.; Falconieri, V.; Rao, P.; Davis, M. I.; Pragani, R.; Boxer, M. B.; Earl, L. A.; Milne, J. L. S.; Subramaniam, S. Breaking Cryo-EM Resolution Barriers to Facilitate Drug Discovery. *Cell* **2016**, *165*, 1698–1707.
- (66) Zan, R.; Ramasse, Q. M.; Jalil, R.; Georgiou, T.; Bangert, U.; Novoselov, K. S. Control of Radiation Damage in MoS₂ by Graphene Encapsulation. *ACS Nano* **2013**, *7*, 10167–10174.
- (67) Al Balushi, Z. Y.; Wang, K.; Ghosh, R. K.; Vilá, R. A.; Eichfeld, S. M.; Caldwell, J. D.; Qin, X.; Lin, Y.-C.; DeSario, P. A.; Stone, G.; Subramanian, S.; Paul, D. F.; Wallace, R. M.; Datta, S.; Redwing, J. M.; Robinson, J. A. Two-Dimensional Gallium Nitride Realized via Graphene Encapsulation. *Nat. Mater.* **2016**, *15*, 1166–1171.
- (68) Jiang, L.; Shi, Z.; Zeng, B.; Wang, S.; Kang, J.-H.; Joshi, T.; Jin, C.; Ju, L.; Kim, J.; Lyu, T.; Shen, Y.-R.; Crommie, M.; Gao, H.-J.; Wang, F. Soliton-Dependent Plasmon Reflection at Bilayer Graphene Domain Walls. *Nat. Mater.* **2016**, *15*, 840–844.
- (69) Matyjaszewski, K.; Xia, J. Atom Transfer Radical Polymerization. *Chem. Rev.* **2001**, *101*, 2921–2990.
- (70) Moad, G.; Rizzardo, E.; Thang, S. H. Radical Addition–fragmentation Chemistry in Polymer Synthesis. *Polymer* **2008**, *49*, 1079–1131.
- (71) Smith, B. J.; Dichtel, W. R. Mechanistic Studies of Two-Dimensional Covalent Organic Frameworks Rapidly Polymerized from Initially Homogenous Conditions. *J. Am. Chem. Soc.* **2014**, *136*, 8783–8789.
- (72) Smith, B. J.; Hwang, N.; Chavez, A. D.; Novotney, J. L.; Dichtel, W. R. Growth Rates and Water Stability of 2D Boronate Ester Covalent Organic Frameworks. *Chem. Commun.* **2015**, *51*, 7532–7535.
- (73) Calik, M.; Sick, T.; Dogru, M.; Döblinger, M.; Datz, S.; Budde, H.; Hartschuh, A.; Auras, F.; Bein, T. From Highly Crystalline to Outer Surface-Functionalized Covalent Organic Frameworks—A Modulation Approach. *J. Am. Chem. Soc.* **2016**, *138*, 1234–1239.
- (74) Smith, B. J.; Overholts, A. C.; Hwang, N.; Dichtel, W. R. Insight into the Crystallization of Amorphous Imine-Linked Polymer Networks to 2D Covalent Organic Frameworks. *Chem. Commun.* **2016**, *52*, 3690–3693.
- (75) Ascherl, L.; Sick, T.; Margraf, J. T.; Lapidus, S. H.; Calik, M.; Hettstedt, C.; Karaghiosoff, K.; Döblinger, M.; Clark, T.; Chapman, K. W.; Auras, F.; Bein, T. Molecular Docking Sites Designed for the Generation of Highly Crystalline Covalent Organic Frameworks. *Nat. Chem.* **2016**, *8*, 310–316.
- (76) Dalapati, S.; Jin, E.; Addicoat, M.; Heine, T.; Jiang, D. Highly Emissive Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2016**, *138*, 5797–5800.
- (77) Chen, X.; Addicoat, M.; Irle, S.; Nagai, A.; Jiang, D. Control of Crystallinity and Porosity of Covalent Organic Frameworks by Managing Interlayer Interactions Based on Self-Complementary π -Electronic Force. *J. Am. Chem. Soc.* **2013**, *135*, 546–549.
- (78) Matsumoto, M.; Dasari, R. R.; Ji, W.; Feriante, C. H.; Parker, T. C.; Marder, S. R.; Dichtel, W. R. Rapid, Low Temperature Formation of Imine-Linked COFs Catalyzed by Metal Triflates. *J. Am. Chem. Soc.* **2017**, *139*, 4999–5002.
- (79) Vazquez-Molina, D. A.; Mohammad-Pour, G. S.; Lee, C.; Logan, M. W.; Duan, X.; Harper, J. K.; Uribe-Romo, F. J. Mechanically Shaped Two-Dimensional Covalent Organic Frameworks Reveal Crystallographic Alignment and Fast Li-Ion Conductivity. *J. Am. Chem. Soc.* **2016**, *138*, 9767–9770.
- (80) Wan, S.; Guo, J.; Kim, J.; Ihee, H.; Jiang, D. A Photoconductive Covalent Organic Framework: Self-Condensed Arene Cubes Composed of Eclipsed 2D Polypyrene Sheets for Photocurrent Generation. *Angew. Chem., Int. Ed.* **2009**, *48*, 5439–5442.
- (81) Colson, J. W.; Woll, A. R.; Mukherjee, A.; Levendorf, M. P.; Spitler, E. L.; Shields, V. B.; Spencer, M. G.; Park, J.; Dichtel, W. R. Oriented 2D Covalent Organic Framework Thin Films on Single-Layer Graphene. *Science* **2011**, *332*, 228–231.

- (82) Medina, D. D.; Werner, V.; Auras, F.; Tautz, R.; Dogru, M.; Schuster, J.; Linke, S.; Döblinger, M.; Feldmann, J.; Knochel, P.; Bein, T. Oriented Thin Films of a Benzodithiophene Covalent Organic Framework. *ACS Nano* **2014**, *8*, 4042–4052.
- (83) Calik, M.; Auras, F.; Salonen, L. M.; Bader, K.; Grill, I.; Handloser, M.; Medina, D. D.; Dogru, M.; Löbermann, F.; Trauner, D.; Hartschuh, A.; Bein, T. Extraction of Photogenerated Electrons and Holes from a Covalent Organic Framework Integrated Heterojunction. *J. Am. Chem. Soc.* **2014**, *136*, 17802–17807.
- (84) Colson, J. W.; Mann, J. A.; DeBlase, C. R.; Dichtel, W. R. Patterned Growth of Oriented 2D Covalent Organic Framework Thin Films on Single-Layer Graphene. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 378–384.
- (85) Gou, X.; Zhang, Q.; Wu, Y.; Zhao, Y.; Shi, X.; Fan, X.; Huang, L.; Lu, G. Preparation and Engineering of Oriented 2D Covalent Organic Framework Thin Films. *RSC Adv.* **2016**, *6*, 39198–39203.
- (86) Bisbey, R. P.; DeBlase, C. R.; Smith, B. J.; Dichtel, W. R. Two-Dimensional Covalent Organic Framework Thin Films Grown in Flow. *J. Am. Chem. Soc.* **2016**, *138*, 11433–11436.
- (87) Feldblyum, J. I.; McCreery, C. H.; Andrews, S. C.; Kurosawa, T.; Santos, E. J. G.; Duong, V.; Fang, L.; Ayzner, A. L.; Bao, Z. Few-Layer, Large-Area, 2D Covalent Organic Framework Semiconductor Thin Films. *Chem. Commun.* **2015**, *51*, 13894–13897.
- (88) Kandambeth, S.; Venkatesh, V.; Shinde, D. B.; Kumari, S.; Halder, A.; Verma, S.; Banerjee, R. Self-Templated Chemically Stable Hollow Spherical Covalent Organic Framework. *Nat. Commun.* **2015**, *6*, 6786.
- (89) Smith, B. J.; Parent, L. R.; Overholts, A. C.; Beaucage, P. A.; Bisbey, R. P.; Chavez, A. D.; Hwang, N.; Park, C.; Evans, A. M.; Gianneschi, N. C.; Dichtel, W. R. Colloidal Covalent Organic Frameworks. *ACS Cent. Sci.* **2017**, *3*, 58–65.
- (90) Tan, J.; Namuangruk, S.; Kong, W.; Kungwan, N.; Guo, J.; Wang, C. Manipulation of Amorphous-to-Crystalline Transformation: Towards the Construction of Covalent Organic Framework Hybrid Microspheres with NIR Photothermal Conversion Ability. *Angew. Chem., Int. Ed.* **2016**, *55*, 13979–13984.
- (91) Nicolosi, V.; Chhowalla, M.; Kanatzidis, M. G.; Strano, M. S.; Coleman, J. N. Liquid Exfoliation of Layered Materials. *Science* **2013**, *340*, 1226419.
- (92) Berlanga, I.; Ruiz-González, M. L.; González-Calbet, J. M.; Fierro, J. L. G.; Mas-Ballesté, R.; Zamora, F. Delamination of Layered Covalent Organic Frameworks. *Small* **2011**, *7*, 1207–1211.
- (93) Bunck, D. N.; Dichtel, W. R. Bulk Synthesis of Exfoliated Two-Dimensional Polymers Using Hydrazone-Linked Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2013**, *135*, 14952–14955.
- (94) Chandra, S.; Kandambeth, S.; Biswal, B. P.; Lukose, B.; Kunjir, S. M.; Chaudhary, M.; Babarao, R.; Heine, T.; Banerjee, R. Chemically Stable Multilayered Covalent Organic Nanosheets from Covalent Organic Frameworks via Mechanical Delamination. *J. Am. Chem. Soc.* **2013**, *135*, 17853–17861.
- (95) Berlanga, I.; Mas-Ballesté, R.; Zamora, F. Tuning Delamination of Layered Covalent Organic Frameworks through Structural Design. *Chem. Commun.* **2012**, *48*, 7976–7978.
- (96) Khayum, M. A.; Kandambeth, S.; Mitra, S.; Nair, S. B.; Das, A.; Nagane, S. S.; Mukherjee, R.; Banerjee, R. Chemically Delaminated Free-Standing Ultrathin Covalent Organic Nanosheets. *Angew. Chem., Int. Ed.* **2016**, *55*, 15604–15608.
- (97) Li, G.; Zhang, K.; Tsuru, T. Two-Dimensional Covalent Organic Framework (COF) Membranes Fabricated via the Assembly of Exfoliated COF Nanosheets. *ACS Appl. Mater. Interfaces* **2017**, *9*, 8433–8436.
- (98) Kang, Z.; Peng, Y.; Qian, Y.; Yuan, D.; Addicoat, M. A.; Heine, T.; Hu, Z.; Tee, L.; Guo, Z.; Zhao, D. Mixed Matrix Membranes (MMMs) Comprising Exfoliated 2D Covalent Organic Frameworks (COFs) for Efficient CO₂ Separation. *Chem. Mater.* **2016**, *28*, 1277–1285.
- (99) Mitra, S.; Kandambeth, S.; Biswal, B. P.; Khayum, M. A.; Choudhury, C. K.; Mehta, M.; Kaur, G.; Banerjee, S.; Prabhune, A.; Verma, S.; Roy, S.; Kharul, U. K.; Banerjee, R. Self-Exfoliated Guanidinium-Based Ionic Covalent Organic Nanosheets (iCONs). *J. Am. Chem. Soc.* **2016**, *138*, 2823–2828.
- (100) Mitra, S.; Sasmal, H. S.; Kundu, T.; Kandambeth, S.; Illath, K.; Díaz Díaz, D.; Banerjee, R. Targeted Drug Delivery in Covalent Organic Nanosheets (CONs) via Sequential Postsynthetic Modification. *J. Am. Chem. Soc.* **2017**, *139*, 4513–4520.
- (101) Larrea, C. R.; Baddeley, C. J. Fabrication of a High-Quality, Porous, Surface-Confined Covalent Organic Framework on a Reactive Metal Surface. *ChemPhysChem* **2016**, *17*, 971–975.
- (102) Faury, T.; Clair, S.; Abel, M.; Dumur, F.; Gignes, D.; Porte, L. Sequential Linking To Control Growth of a Surface Covalent Organic Framework. *J. Phys. Chem. C* **2012**, *116*, 4819–4823.
- (103) Shi, K. J.; Zhang, X.; Shu, C. H.; Li, D. Y.; Wu, X. Y.; Liu, P. N. Ullmann Coupling Reaction of Aryl Chlorides on Au(111) Using Dosed Cu as a Catalyst and the Programmed Growth of 2D Covalent Organic Frameworks. *Chem. Commun.* **2016**, *52*, 8726–8729.
- (104) Shi, K. J.; Yuan, D. W.; Wang, C. X.; Shu, C. H.; Li, D. Y.; Shi, Z. L.; Wu, X. Y.; Liu, P. N. Ullmann Reaction of Aryl Chlorides on Various Surfaces and the Application in Stepwise Growth of 2D Covalent Organic Frameworks. *Org. Lett.* **2016**, *18*, 1282–1285.
- (105) Marele, A. C.; Mas-Ballesté, R.; Terracciano, L.; Rodríguez-Fernández, J.; Berlanga, I.; Alexandre, S. S.; Otero, R.; Gallego, J. M.; Zamora, F.; Gómez-Rodríguez, J. M. Formation of a Surface Covalent Organic Framework Based on Polyester Condensation. *Chem. Commun.* **2012**, *48*, 6779–6781.
- (106) Dienstmaier, J. F.; Gigler, A. M.; Goetz, A. J.; Knochel, P.; Bein, T.; Lyapin, A.; Reichlmaier, S.; Heckl, W. M.; Lackinger, M. Synthesis of Well-Ordered COF Monolayers: Surface Growth of Nanocrystalline Precursors versus Direct On-Surface Polycondensation. *ACS Nano* **2011**, *5*, 9737–9745.
- (107) Guan, C.-Z.; Wang, D.; Wan, L.-J. Construction and Repair of Highly Ordered 2D Covalent Networks by Chemical Equilibrium Regulation. *Chem. Commun.* **2012**, *48*, 2943–2945.
- (108) Liu, X.-H.; Guan, C.-Z.; Ding, S.-Y.; Wang, W.; Yan, H.-J.; Wang, D.; Wan, L.-J. On-Surface Synthesis of Single-Layered Two-Dimensional Covalent Organic Frameworks via Solid–Vapor Interface Reactions. *J. Am. Chem. Soc.* **2013**, *135*, 10470–10474.
- (109) Xu, L.; Zhou, X.; Yu, Y.; Tian, W. Q.; Ma, J.; Lei, S. Surface-Confined Crystalline Two-Dimensional Covalent Organic Frameworks via on-Surface Schiff-Base Coupling. *ACS Nano* **2013**, *7*, 8066–8073.
- (110) Liu, C.; Yu, Y.; Zhang, W.; Zeng, Q.; Lei, S. Room-Temperature Synthesis of Covalent Organic Frameworks with a Boronic Ester Linkage at the Liquid/Solid Interface. *Chem. - Eur. J.* **2016**, *22*, 18412–18418.
- (111) Liu, C.; Zhang, W.; Zeng, Q.; Lei, S. A Photoresponsive Surface Covalent Organic Framework: Surface-Confined Synthesis, Isomerization, and Controlled Guest Capture and Release. *Chem. - Eur. J.* **2016**, *22*, 6768–6773.
- (112) Dai, W.; Shao, F.; Szczerbiński, J.; McCaffrey, R.; Zenobi, R.; Jin, Y.; Schlüter, A. D.; Zhang, W. Synthesis of a Two-Dimensional Covalent Organic Monolayer through Dynamic Imine Chemistry at the Air/Water Interface. *Angew. Chem., Int. Ed.* **2016**, *55*, 213–217.
- (113) Sahabudeen, H.; Qi, H.; Glatz, B. A.; Tranca, D.; Dong, R.; Hou, Y.; Zhang, T.; Kuttner, C.; Lehnert, T.; Seifert, G.; Kaiser, U.; Fery, A.; Zheng, Z.; Feng, X. Wafer-Sized Multifunctional Polyimide-Based Two-Dimensional Conjugated Polymers with High Mechanical Stiffness. *Nat. Commun.* **2016**, *7*, 13461.