Chemical Control over Nucleation and Anisotropic Growth of Two-Dimensional Covalent Organic Frameworks

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ABSTRACT: Two-dimensional covalent organic frameworks (2D COFs) are composed of structurally precise, permanently porous, layered polymer sheets. 2D COFs have traditionally been synthesized as polycrystalline aggregates with small crystalline domains. Only recently have a small number of 2D COFs been obtained as single crystals, which were prepared by a seeded growth approach via the slow introduction of monomers, which favored particle growth over nucleation. However, these procedures are slow and operationally difficult, making it desirable to develop polymerization methods that do not require the continuous addition of reactants over days or weeks. Here, we achieve the rapid growth of boronate ester-linked COFs by chemically suppressing nucleation via addition of an excess of a monofunctional competitor, 4-tert-butylcatechol (TCAT), into the polymerization. In situ X-ray scattering measurements show that TCAT suppresses colloid nucleation, which enables seeded growth polymerizations in the presence of high monomer concentrations. Kinetic Monte Carlo simulations reveal that TCAT limits oligomers to sizes below the critical nucleus size and that in-plane expansion is restricted compared to out-of-plane oriented attachment of oligomers. The simulations are consistent with transmission electron micrographs, which show that the particles grow predominantly in the stacking direction. This mechanistic insight into the role of the modulators in 2D polymerizations enables the size and aspect ratio of COF colloids to be controlled under operationally simple conditions. This chemically controlled growth strategy will accelerate the discovery and exploration of COF materials and their emergent properties.

INTRODUCTION

The polymerization of monomers into periodic two-dimensional (2D) networks produces covalently linked sheets, which provide combinations of properties not found in traditional polymer architectures.1–3 For example, 2D covalent organic frameworks (COFs) feature precise monomer arrangements and permanent porosity,4–6 which make them of interest for applications including energy storage,7,8 catalysis,9 membranes,10–13 chemical separations,11 and organic electronic devices.14–16 Despite the potential of these materials, most 2D COFs are isolated as insoluble powders with small crystalline domains, typically on the order of 50 nm for the in-plane dimension and far less for the out-of-plane, which limits their relevance for otherwise promising applications.4,17,18 In previous mechanistic studies of COF polymerization, Smith et al. identified an irreversible precipitation in boronate ester-linked systems that prevented further crystallite growth.17 This drawback was later overcome by including nitrile cosolvents, which prevented aggregation and provided colloidal suspensions of COF nanoparticles (Figure 1).19 These colloids were then grown into micron-sized single crystals by the slow addition of monomers (Figure 1).20 By limiting the steady-state concentration of monomers, nucleation of new particles was suppressed, and addition to the preformed colloid seeds dominated the polymerization process.18 Despite this...
Dichtel and co-workers demonstrated that monofunctional nucleation size. These experiments unambiguously demonstrated an average size of oligomers in solution to lower than the critical KMC simulations, which show that modulators limit the colloid nucleation without shutting down the seeded growth of TCAT to COF monomer solutions decreases the rate of scattering and DLS measurements revealed that addition of monofunctional species, or modulating agents, in butylcatechol (TCAT), to the polymerization (Figure 1). The addition of monofunctional modulators can lead to significant internal functionalization of boronate ester-linked 3D COF powders.

Additionally, Dichtel and co-workers have shown that, in 3D systems, inclusion of partially truncated monomers or monofunctional modulators can lead to significant internal functionalization of boronate ester-linked 3D COF powders. More recently, this modulation concept has been successfully implemented in 3D imine-linked systems and provided the first imine-linked 3D COF single crystals. However, the effect of modulators on the nucleation and growth processes of 2D COFs is not well-understood. To deconvolute the effect of TCAT on nucleation and growth, a reaction pathway analysis suggests that the addition of modulators might change the relative rates of growth in the in-plane (covalent bonding) and out-of-plane (stacking) directions such that the particles grow preferentially in the stacking direction. While preferential growth is not easily characterized in polycrystalline powder products, this effect is confirmed by TEM of the COF colloids grown in the presence of TCAT, which are primarily elongated by oriented attachment of oligomers in the out-of-plane (stacking) direction. This approach represents the first example of anisotropically manipulating 2D polymer growth along a specific crystalline direction. Furthermore, previous 2D COF syntheses have involved empirical optimization and parallel experiments that have traditionally identified conditions with uncontrolled nucleation. This controlled nucleation approach identifies conditions that are amenable to parallelization, which will dramatically simplify and accelerate the discovery and optimization of functional 2D COF systems.

**RESULTS AND DISCUSSION**

The addition of a monofunctional catechol, TCAT, to 2D COF polymerizations suppresses colloid nucleation in a concentration-dependent manner. TCAT, which we previously used to slow COF precipitation, was chosen as the modulating agent (Figure S9) because both TCAT itself and its boronate ester-linked oligomers are highly soluble in the polymerization solvent. Monomer solutions of 2,3,6,7,10,11-hexahydroxystriphenylene (HHTP, 2 mM) and 1,4-phenylenebis(boronic acid) (PBBA, 3 mM) in CH$_3$CN:1,4-dioxane:mesitylene (80/16/4 v/v/v) were prepared, and variable amounts of TCAT (equiv = [TCAT]/[PBBA]) were added to these solutions (Figure 2A). In situ small-angle and wide-angle X-ray scattering (SAXS/WAXS) techniques were used to slow COF precipitation, without eliminating seeded growth.

The addition of a modulator in the seeded growth mixture produces large, high-quality 2D COF particles, as determined by in situ X-ray scattering, ¹H NMR spectroscopy, nitrogen sorption, and transmission electron microscopy (TEM). We hypothesized that the addition of a monofunctional modulating agent would dynamically cap the growing colloid particles, thus promoting the exchange of reversible bonds and the growth of the colloids over the formation of new nuclei (Figure 1). Furthermore, KMC simulations combined with previous reaction pathway analysis suggest that the addition of modulators might change the relative rates of growth in the in-plane (covalent bonding) and out-of-plane (stacking) directions such that the particles grow preferentially in the stacking direction. While preferential growth is not easily characterized in polycrystalline powder products, this effect is confirmed by TEM of the COF colloids grown in the presence of TCAT, which are primarily elongated by oriented attachment of oligomers in the out-of-plane (stacking) direction. This approach represents the first example of anisotropically manipulating 2D polymer growth along a specific crystalline direction. Furthermore, previous 2D COF syntheses have involved empirical optimization and parallel experiments that have traditionally identified conditions with uncontrolled nucleation. This controlled nucleation approach identifies conditions that are amenable to parallelization, which will dramatically simplify and accelerate the discovery and optimization of functional 2D COF systems.

![Figure 1. Schematic of 2D polymerization approaches. Monomers nucleate to form 2D colloidal seeds (left). Pre-existing COF colloid seeds can be grown via slow addition of monomers to seeds resulting in slow, rate controlled growth (top right) or instantaneous addition of monomers resulting in rapid, chemically controlled growth (bottom right).](image-url)
used to identify the nucleation of COF-5 colloids. SAXS experiments monitored at 70 °C for 60 min show that TCAT loadings of 0, 3, and 5 equiv fail to suppress nucleation, as made evident by the increase in intensity and shift of the traces to less negative log(Q space) values, which indicates larger particle size (Figure 2B, Figure S5). In contrast, SAXS traces of reaction mixtures containing 10 and 15 equiv of TCAT show little to no change over the same time period, suggesting that large species are not formed and therefore that nucleation is suppressed (Figure 2B). To determine the occurrence and rate of COF nucleation, we monitored the intensity of the COF-5 (100) Bragg diffraction peak (Q = 0.24 Å⁻¹) over time (Figure S5). As the TCAT loading increased from 0 to 15 equiv, this diffraction peak appeared more slowly and was not observed after 60 min for the 10 and 15 equiv conditions, which is consistent with the SAXS data (Figure 2C). To examine the extent of nucleation suppression with a 15 equiv TCAT loading, we continued to heat our modulated monomer solution at 70 °C for 48 h. By comparing the WAXS traces (Figure 2D) to that of monomer without added modulator, we can clearly see the absence of a (100) Bragg diffraction peak even after 48 h of heating, suggesting that 15 equiv of TCAT effectively suppresses colloid nucleation over longer periods than the typical minutes-long COF-5 colloid polymerization time. Additionally, ¹H NMR time course experiments of the reaction mixture with 15 equiv of TCAT display the formation of small PBBA−TCAT oligomers and limited change in HHTP intensity over 48 h, further indicating that nucleation is suppressed (Figure S15 and Table S2).

Having identified conditions that suppress COF-5 nucleation, we tested whether we could use TCAT in seeded growth experiments to enlarge existing 2D COF colloids while still suppressing the formation of new particles. First, we prepared COF-5 colloidal seeds by heating HHTP (2 mM) and PBBA (3 mM) to 70 °C in CH₂CN:1,4-dioxane:mesitylene (80/16/4 v/v/v) for 24 h. Then, we transferred the nanoparticle solution into new vials and introduced solutions containing additional monomers with 15 equiv of TCAT (Figure 3A). By varying the monomer concentration, we were able to vary the molar equivalents of the monomers added relative to those present in the initial colloids from 0 to 4.5 equiv (equiv = [HHTP added]/[HHTP in the COF-5 seed solution]) while also maintaining a consistent dilution ratio of the COF seeds. For a fixed heating time of 48 h we monitored the (100) WAXS peak as a function of the amount of added monomer. The diffraction peak increased in intensity and sharpened, indicating that the size of the COF-5 crystalline domains increased during the seeded growth polymerizations (Figure 3B). This observation is consistent with dynamic light scattering (DLS) experiments, which show an increase in average particle size from 60 to 450 nm along with monomodal size distributions as a function of the amount of added monomer (Figure 3C). Monitoring seeded growth polymerizations as a function of reaction time showed an increase in crystallinity and particle size over the course of 2 days, after which no change was observed. For a fixed monomer addition of 4.5 equiv, the (100) WAXS peak intensifies and sharpens over the course of 48 h, meaning that both the amount of added monomer and the reaction time affect the crystallinity of the colloid nanoparticles (Figure 3D). DLS analysis provided monomodal distributions and a steady increase in the colloid size over time, which is consistent with the WAXS experiments and indicates that the growth process occurs over 48 h (Figure 3E). These findings demonstrate that TCAT both suppresses particle nucleation yet still permits the enlargement of preformed COF colloids.

The seeded growth approach provides COF-5 samples with high materials quality, as judged by Brunauer−Emmett−Teller (S_BET) surface area. The colloids from the COF-5 growth experiments were collected via centrifugation, washed with clean solvent, and dried under vacuum overnight. Nitrogen sorption isotherms were collected and show that the COF-5 seeds have a Brunauer−Emmett−Teller (S_BET) surface area of 1740 m² g⁻¹. After a 48 h modulated growth with 15 equiv of TCAT and 1.1, 3.4, or 4.5 equiv of monomer added to the reaction mixtures, S_BET increased to 1930, 1950, and 1990 m² g⁻¹, respectively (Figure 3F, Figure S19). In all cases S_BET approached the theoretical Connolly surface area of 2000 m² g⁻¹ for COF-5. Additionally, nonlocal density functional theory (NLDFT) analysis indicated that all of the samples had narrow pore width distributions that are consistent with the expected pore size of 27 Å (Figure 3G). These observations indicate that the presence of TCAT does not disrupt the formation of high-quality samples of COF-5 with high surface area and uniform porosity.

¹H NMR spectroscopy of components of the reaction mixture confirms that, despite being present in the polymerization mixture in large excess relative to the COF monomers, almost no TCAT is incorporated into the 2D COF product. To determine the amount of TCAT incorporated into the
COF, we isolated the COF colloids, degraded them to soluble products in the presence of pinacol, and analyzed the relative amounts of HHTP and TCAT by $^1$H NMR spectroscopy (Figure S14 and Table S1). Separately, the compositions of the soluble components of the polymerization mixture were also characterized. The $^1$H NMR spectrum of the postpolymerization solution was dominated by TCAT and contained very little HHTP (0.03:1.00 HHTP:TCAT ratio), further indicating that the polymerization is nearly complete after 48 h. In contrast, the COF-5 samples were dominated by HHTP and contained almost no TCAT (1.00:0.04 HHTP:TCAT ratio). The low TCAT incorporation suggests that TCAT does not introduce defects into the final 2D COF structure. We speculate that the small amount found in the COF samples corresponds to TCAT bound to dangling boronic esters at the edges of the particles, which is consistent with previous reports.

To gain mechanistic insight into how TCAT affects COF nucleation and growth processes, we employed kinetic Monte Carlo (KMC) simulations that have been previously developed to study the formation of COF-5 based on microscopic rate parameters. By considering microscopic processes such as bond formation and breakage, the KMC model reproduces characteristics of experimental COF formation, including the rate orders of nucleation and growth. Here, we modified the KMC model to study the early stage of nucleation by considering the oligomerization of HHTP and PBBA in the presence of TCAT. For these simulations we have excluded the more complex process of stacking among oligomers; as such, the simulation results should not be used to interpret those processes. We first focused on the evolution of the average oligomer size in solution for different amounts of TCAT added to the monomer solutions (Figure 4A, Figure S22). TCAT slows the elongation of oligomers and limits them to small sizes, which is consistent with the SAXS/WAXS data (Figure 2, Figure S21). Excess TCAT molecules react with the PBBA units and prevent further growth of the oligomer when present, which decreases the average oligomer size (Figure S23). Likewise, the maximum oligomer size, which is relevant to the nucleation rate, also decreases as a function of added TCAT (Figure 4B). With 15 equiv of TCAT, the oligomers do not exceed 7 monomer units throughout the 60 min simulation. This size is close to the critical nucleus (in-plane) size (consisting of 6−7 monomers) found in our previous KMC simulations and is consistent with the experimental observations of suppressed nucleation by $^1$H NMR and in situ X-ray scattering. This result indicates that TCAT prevents...
COF nucleation from occurring but favors the formation of small oligomers.

Although it is not straightforward to use the present KMC model to simulate the growth of COF crystals in the presence of TCAT, the KMC results above, combined with previous theoretical analysis, provide insight into the impact of TCAT on the COF growth process. Molecular dynamics simulations and reaction pathway analyses have shown that stacking both stabilizes the planar structure of 2D COFs and inhibits depolymerization. In addition to limiting nucleation, TCAT can limit the relative rates of in-plane and out-of-plane growth, which control the shape and aspect ratios of the resulting COF nanoparticles. One possibility is that TCAT reacts with dangling boronic acid units in COF crystals and must be hydrolyzed or exchanged for HHTP to extend the lattice in-plane. This capping of boronic acids would be expected to influence the size and shape of the growing crystallites, since it would slow in-plane growth and the formation of new layers. Additionally, TCAT does not destabilize COF crystals by exchanging into the already formed boronate esters within the COF-5 lattice since bond breakage is prohibitive inside a crystal. The high materials quality and low incorporation of TCAT into COF-5 are both consistent with the above conclusions (Figure 3F, Figure S14). Furthermore, no change in particle size or crystallinity was observed when COF colloids were heated in the presence of 15 equiv of TCAT for 48 h (Figures S3 and S10). These combined observations suggest that TCAT is only reactive with boronic acids in monomers, in oligomers, and at the edges of crystals and does not undergo transesterification with boronate esters in the layered COF structure.

TEM analysis of COF-5 demonstrates that the particles grow anisotropically but are still highly crystalline with lattice fringes extending throughout the particles. TEM images of the COF-5 colloids used as seeds display layered particles that are approximately 50 nm in diameter, which matches the size measured by DLS (Figure 5A, Figure S2). These particles show the expected hexagonal lattice fringes, as made evident by
the 6-fold symmetry in their fast Fourier transform (FFT) patterns. The COF-5 particles grown by adding 4.5 equiv of monomer and 15 equiv of TCAT ranged in size from 420 to 490 nm and were observed at random orientations on the TEM grid. Lattice-resolution images of the individual COF-5 particles show that they are highly crystalline with consistent lattice fringes that extend throughout the particles (Figure 5B). Consistent with our KMC analysis, images of the COF particles display that they are growing preferentially in the out-of-plane direction compared to the in-plane direction. For the particle shown, the fringe spacing is ~27 Å (fitting d_{100} for COF-5) as measured by the FFT, which is consistent with the predicted lattice spacing for viewing the stacked particles from a side-on orientation (Figure 5C, Figures S28 and S29). The ability to control the preferred growth of COF colloids along a crystalline axis could enhance optoelectronic properties, such as exciton diffusion, or enable anisotropic orientation of guest molecules. For these reasons, this oriented attachment growth mechanism warrants further TEM experiments as well as additional simulations to elucidate the microscale processes responsible for this anisotropic growth.

With this understanding of the role that TCAT plays in COF-5 nucleation and growth mechanisms, we evaluated the generality of this modulated growth approach for other boronate ester-linked 2D COFs. We studied three other boronate ester-linked 2D COFs: TP-COF, DPB-COF, and COF-10 which are synthesized by the condensation of HHTP with 2,7-pyrenebis(boronic acid), 4,4′-diphenylbutadiynebis(boronic acid), and 4,4′-biphenylbis(boronic acid), respectively. TP-COF, DPB-COF, and COF-10 all exhibited similar nucleation suppression and colloid growth behavior as COF-5, with 15 equiv of TCAT suppressing nucleation for at least several hours (Figures S7 and S8). For all COFs, colloid seeds were first synthesized by heating HHTP (2 mM) and the corresponding boronic acid (3 mM) in CH₃CN:1,4-dioxane:mesitylene (80/16/4 v/v/v) for 24 h at 70 °C. We then placed the COF colloid seeds in vials and instantaneously added 9 equiv of monomer and 15 equiv of TCAT. By monitoring the (100) WAXS peak (Q = 0.16 Å⁻¹ for DPB-COF, Q = 0.19 Å⁻¹ for TP-COF, and Q = 0.20 Å⁻¹) as a function of the amount of time spent heating at 70 °C for a fixed monomer addition amount of 9 equiv, we observed that the (100) peak sharpened and increased in intensity, indicating that the added monomers attached to and increased the pre-existing COF colloid domains (Figure 6A–C). This conclusion is supported by DLS, which shows that the size distributions remained monomodal as the particle size increased. The DLS-measured average particle size of the TP-COF colloids shifts from 110 to 1400 nm after 8 h of heating (Figure 6D), that of DPB-COF from 90 to 260 nm after 4 h of heating (Figure 6E), and that of COF-10 from 110 to 800 nm after 8 h of heating (Figure 6F). Taken together, these results demonstrate that modulated growth conditions suppress nucleation, such that preformed COF colloids can be enlarged by increasing the amount of added monomers or the reaction time.

Safety Statement. No unexpected or unusually high safety hazards were encountered.

CONCLUSIONS

We have developed a chemically controlled approach to rapidly grow large, highly crystalline 2D COF colloids under operationally simple and scalable conditions. In situ X-ray scattering experiments demonstrate that a monofunctional additive, TCAT, suppresses colloid nucleation for longer than typical COF colloid polymerization times. By adding TCAT to preformed colloids in the presence of monomers, the size and the overall crystallinity of the pre-existing COF particles increase, as made evident by in situ X-ray scattering and DLS measurements. These findings are substantiated by KMC simulations that provide mechanistic insight into the role TCAT plays in the elongation of oligomers. By limiting the average oligomer size to below the critical nucleus size, nucleation is suppressed at high TCAT loading while crystal growth remains possible. However, the slowed in-plane expansion results in anisotropic COF growth, as made evident by TEM. Nitrogen sorption and diffraction measurements indicate that the grown colloids are of exceptionally high quality with minimal TCAT incorporation. We find that this chemically controlled nucleation and growth procedure is...
Collaborative Access Team (DND-CAT) located at Sector 5 demonstrated here will enable the more efficient investigation of possible COF structures and study of their emergent properties for use in a variety of applications.

**ASSOCIATED CONTENT**

2 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.9b00944.

Materials and methods, experimental procedures, dynamic light scattering experiments, in situ X-ray scattering experiments, optical images of COF-5 growth solutions, nuclear magnetic resonance spectra, Fourier-transform infrared spectroscopy, powder X-ray diffraction, nitrogen sorption isotherms, pore width distributions, BET plots, kinetic Monte Carlo simulations, transmission electron microscopy images, and in situ X-ray scattering experiments of additional modulators tested (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Science Foundation (NSF) through the Northwestern Materials Research Science and Engineering Center, under NSF Award DMR-1720139 and by the Army Research Office, under the Multidisciplinary University Research Initiative (MURI) program, Award W911NF-15-1-0447, and under Grant W911NF-17-1-0339. I.C. and M.J.S. are supported by the NSF Graduate Research Fellowship under Grant (DGE-1324585). Parts of this work were performed at the DuPont–Northwestern–Dow Collaborative Access Team (DND-CAT) located at Sector 5 of the Advanced Photon Source (APS). DND-CAT is supported by Northwestern University, E.I. DuPont de Nemours & Co., and the Dow Chemical Company. This research used resources of the Advanced Photon Source and Center for Nanoscale Materials, both U.S. Department of Energy (DOE) Office of Science User Facilities operated for the DOE Office of Science by Argonne National Laboratory under Contract DE-AC0206CH11357. This work has made use of the IMSERC facility which has received support from the Soft and Hybrid Nanotechnology Experimental (ShyNE) Resource (NSF NNCI-1542205), the State of Illinois, and International Institute for Nanotechnology (IIN). This study also made use of the EPIC facility of NUANCE Center at Northwestern University, which has received support from the Soft and Hybrid Nanotechnology Experimental (ShyNE) Resource (NSF ECCS-1542205), the MRSEC program (NSF DMR-1720139) at the Materials Research Center, the Keck Foundation, the State of Illinois, and International Institute for Nanotechnology (IIN).

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