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Continuous Flow Packed-Bed Reactor**

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COMMUNICATION

Covalent Organic Framework Crystallization using a Continuous Flow Packed-Bed Reactor

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Flow systems enable in-line synthesis and processing of organic materials in a continuous reaction pathway which can be advantageous for high-throughput and scale-up. In this work, a highly crystalline TAPB-OHPDA covalent organic framework (COF) was directly crystallized under continuous flow conditions in as little as 30 minutes. Brunauer, Emmett and Teller (BET) surface analysis reveals high surface areas greater than 1,700 m²/g can be afforded in 2 hours resulting in a 36x faster processing time compared to a majority of other reported solvothermal methods. Additionally, the crystalline COF material was also washed with solvent in flow to reduce the required post-processing burden typically performed iteratively during purification and activation. The results presented herein provide foundational knowledge for COF syntheses under packed-bed flow conditions and reveal an opportunity to accelerate the formation and processing of highly crystalline COF materials.

Covalent organic frameworks (COFs) are a class of exceptionally versatile organic materials that have demonstrated their utility as responsive photodetectors,^{1,2} low-k dielectrics,^{3,4} ultrasensitive optical and electronic sensors,^{5,6} selective gas adsorption materials,^{7–9} high storage electrodes for batteries and supercapacitors,^{10,11} and other emergent applications.^{12,13} Many of these applications take advantage of the properties arising from long range molecular order in the formation of nanoporous two-dimensional (2D) or three-dimensional (3D) structures. In the case of 2D COFs, the organic network is fabricated by selecting linker and vertex monomers with a planar structure that react to form thermodynamically reversible covalent bonds in-plane, and relatively weaker π - π interactions out-of-plane. The resultant structure is highly tuneable and can form pores with various shapes, sizes, and with different framework chemistries and decorated functional groups.^{14,15} This

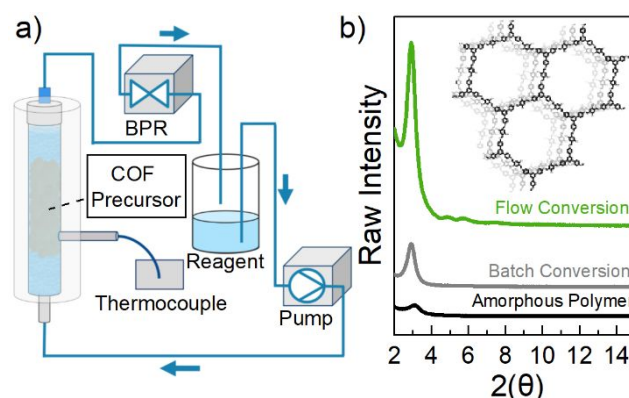


Figure 1. COF Crystallization in Flow (a) Schematic of flow setup; (b) Raw intensity Powder X-ray Diffraction (PXRD) of starting material/COF precursor (black), batch conversion at 70 °C for 17 hours (grey), flow conversion at 70 °C for 17 hours (green)

versatility has become especially valuable in optical applications, where the stacking mode between layers, the molecular chemical makeup, and pore-decorated functional groups have been exploited for bioimaging, photoemission, two-photon absorption, and photoresponsivity.^{16–18}

While the applications and opportunities for crystalline COFs are expanding, the syntheses of high quality powders tend to be time-consuming, with subsequent processing steps often extending over several days as a result of the highly reversible nature of the covalent bonds linking the network together.¹⁹ As such, developing new processes that can enable rapid exploration of COF chemistries and crystallization techniques are of utmost importance to the field.

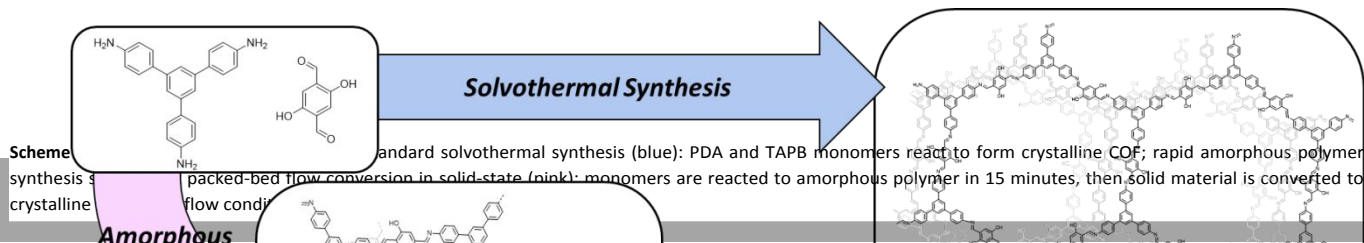
The implementation of flow chemistry, or the use of a continuous reaction rather than traditional batch process, has been leveraged only a few times to prepare COF powders and thin films from monomer solutions. Rodríguez- San-Miguel *et al.*²⁰ first demonstrated the utility of flow processing for COFs by synthesizing imine-based MT-COF-1 under continuous microfluidic conditions with higher crystallinity than the batch synthesized COF.²¹ Peng *et al.* demonstrated the successful synthesis of COFs in flow by injecting monomer solutions into a flow reactor to produce COF-LZU1, with the synthesized COFs exhibiting surface areas comparable to batch-synthesized analogues.²² Bisbey *et al.* demonstrated that maintaining the

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same concentration of oligomers with long induction periods in a flow cell could afford boronate-ester-linked COF films with good crystallinity,²³ while Yang *et al.* revealed that 3D SBFdiyne-COF films could be synthesized using a similar experiment.²⁴ While there are a couple promising examples of continuous flow synthesis of COFs, thus far they have only focused on COF formation occurring from the interaction of monomers in the mobile phase in flow. As a result it can be challenging to find the appropriate conditions that do not clog the reactor as a result of precipitation and COF formation in the line. COF syntheses would therefore benefit from systems that allow for solid-state materials to be reacted in the stationary phase.

This work herein describes a unique continuous flow approach to rapidly produce high quality TAPB-OHPDA COF in a packed-bed flow setup (shown in Figure 1a), through the crystallization of an amorphous polymer precursor in the solid phase. Scheme 1 shows the steps used in this work (pink) to afford crystalline COFs through an initial synthesis of the amorphous polymer followed by subsequent crystallization of the solid material in flow. Compared to the traditional monomer derived single-step solvothermal synthesis (Scheme 1, blue), this two-step flow chemistry process offers unique advantages. In this case, the TAPB-OHPDA COF crystallized in flow, reveals exceptionally high surface areas with values exceeding 1,700 m²/g in as little as 2 hours, representing an exciting opportunity to significantly decrease the synthesis and crystallization time of COF structures while retaining exceptional quality. As imine COFs such as TAPB-OHPDA COF have demonstrated dramatic color changes (orange to dark brown) in the presence of hydrogen-bond-donor solvents and vapors²⁵ as well as enhanced photocatalytic H₂O₂ evolution activity under visible light irradiation, the rapid synthesis described herein will be vital to accelerated material development and process refinement of exciting optical materials.

The amorphous polymer precursor to TAPB-OHPDA COF was synthesized using a modified approach from previous work (see Supporting Information for synthetic details).²⁶ Precursors 1,3,5-*tris*(4-aminophenyl)benzene (TAPB) and 2,5-dihydroxyterephthalaldehyde (OHPDA) were dissolved in a mixture of mesitylene, 1,4-dioxane, and water followed by the addition of acetic acid. After 15 minutes, the amorphous polymer precipitate was collected and washed. This initial rapid synthesis allowed enough time for the dissolved monomers to react and form an orange precipitate, but did not provide sufficient time for the supramolecular assembly to crystallize into a porous framework to form a COF.

Structural and chemical characterization of the amorphous polymer network was carried out using Fourier transform-infrared spectroscopy (FT-IR), Raman spectroscopy, and powder X-ray diffraction (PXRD). Both FT-IR and Raman spectra (further details shown in Figure S6-S7) of the material revealed no remaining starting material and confirm the presence of imine bond formation.^{25,28} Furthermore, PXRD analysis shows a very weak signal at 3.1 2 θ (Figure 1b), indicating that only a very small amount of crystalline material is present. These combined techniques reveal that the synthesized material is in fact a

polymer network connected by imine bonds and is mostly amorphous in nature.

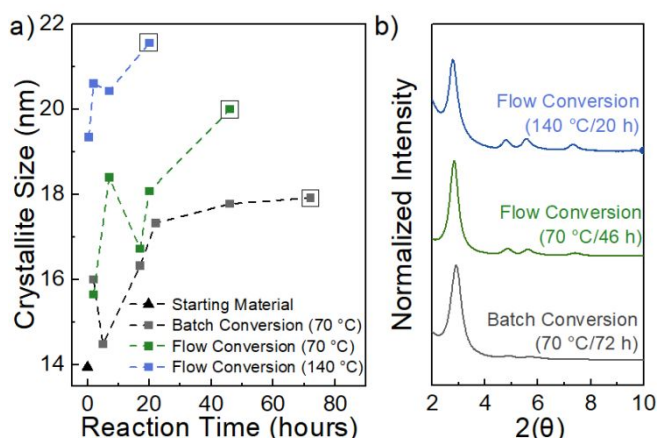


Figure 2. Time and Temperature Dependency of COF Crystallinity in Flow Conversion. (a) Calculated crystallite size for flow and batch conversion (b) PXRD of the best values.

To examine the potential of using continuous flow packed-bed processes to convert this amorphous precursor to crystalline COF, a Vapourtec R-Series Flow Chemistry System was used. In brief, the solid amorphous polymer (80 mg) was loaded into a fixed bed reactor and packed with glass beads to hold the material in place (Figure 1a). Interestingly, we found that solvent recycling was critical for COF conversion and that if the solvent was used in a single pass construct, the amorphous solid slowly degraded into soluble species over time. To better implement this, the reagent inlet and outlet lines were placed in the same vessel to recycle the solvent mixture which was comprised of dioxane, mesitylene, and 10 M acetic acid (6.7:1.7:1, v/v, 8 mL). Solvent flow was conducted using a peristaltic pump at 2.0 mL/min and a thermocouple was used to monitor reactor temperature. A back-pressure regulator (BPR) was placed after the fixed-bed reactor to maintain a system pressure of 5 bar. The temperature was increased by 20 °C intervals every 10 minutes until the bed reactor reached 70 °C. This ensured that no dissolved polymer pieces precipitated within reagent lines upon cooling. The reaction was heated at this temperature for various times (Figure 2, green). At the end of the reaction, the reagent was drained from the fixed bed reactor and the solid material was collected into a vial. Following similar procedures that have yielded high surface area COFs, the material was washed with methanol (20 mL) followed by acetone (20 mL) to remove any portion of the polymer that had dissolved into solution as small molecules.²⁷ Then, methylene chloride (8 mL) was added and left to stand still at RT for 30 min. The solvent was decanted and this step was repeated two more times. Immediately after washing, *n*-hexane (8 mL) was added and left to stand still at room temperature overnight. Finally, this solvent was decanted and the material was placed under N₂ flow and slowly heated (see further details in Supporting Information).

FT-IR and Raman spectroscopy were used to confirm the absence of any remaining starting monomers and the presence of TAPB-OHPDA COF from the flow reaction (Figure S7-S8). PXRD

analysis of this material crystallized in a packed-bed reactor reveals a peak at approximately $2.8\ 2\theta$ that corresponds to the $\langle 100 \rangle$ plane of TAPB-OHPDA COF (Figure 1c) and matches the reported COF PXRD pattern ($2.8\ 2\theta$) synthesized under solvothermal conditions, indicating that both of the materials have the same crystal structure.²⁸ As a comparison, a batch conversion was also tested by heating amorphous material in a scintillation vial to $70\ ^\circ\text{C}$ (Figure 2, gray).

The crystallite size was calculated using the Scherrer equation and is depicted in Figure 2a. A Lorentzian peak fitting program was used to extrapolate the peak position and FWHM of the $\langle 100 \rangle$ peak from all collected data points (see further details in Table S1, Figure S2-S5). Results show that a shortened reaction time of 2 hours at $70\ ^\circ\text{C}$ in flow (green) produces similar sized crystallites to that using the batch conversion method (gray). Running the reaction for 7 hours in flow increases the crystallite size beyond what the batch conversion can achieve after 72 hours. Furthermore, crystallite sizes approaching 20 nm can be formed using flow chemistry and a packed-bed reactor at $70\ ^\circ\text{C}$ after 46 hours.

The flow system allows access to temperatures higher than the solvent boiling point therefore $110\ ^\circ\text{C}$ (see further details in Table S1) and $140\ ^\circ\text{C}$ (Figure 2, blue) reaction temperatures were also tested. Improvement in crystallite size in as little as 30 minutes occurs when converting at $140\ ^\circ\text{C}$. Figure 2b shows the normalized PXRD corresponding to the largest crystallite size of each reaction temperature, with the flow conversion at $140\ ^\circ\text{C}$ clearly showing improvement of weaker diffraction peaks at 4.8, 5.5, and $7.3\ 2\theta$, corresponding to the $\langle 110 \rangle$, $\langle 200 \rangle$, and $\langle 120 \rangle$ planes, respectively.²⁸ This same highly crystalline TAPB-OHPDA COF also exhibits expected strong ultraviolet wavelength absorption and visible-range photoluminescence with a maximum around 420 nm (see details in Figure S8).

A time-consuming part of COF fabrication is the washing step, often employed after synthesis to increase the surface area. Typically during the washing step, the COF material is transferred to new set up and washed with various solvents to remove any starting materials or impurities. In order to facilitate more automated processes without having to remove the solid material, these washing steps were performed in-line directly following the conversion reaction (see details in Figure S1). To accomplish this, after COF crystallization was complete, the reagent outlet was switched to a waste stream and the COF was washed with methanol, acetone, and methylene chloride. Then, the inlet and outlet reagent lines were added to the same vial and *n*-hexane was recycled overnight. After washing, the solvent was removed and the material was collected for the drying and heating step. Analysis of the $\langle 100 \rangle$ peak of this flow washed material indicates a crystallite size of 19.5 nm (Figure 3a), which is in good agreement to the COF crystallized in flow and washed via the traditional batch procedure. The flow system's ability to quickly and efficiently exchange solvents allows for sequential COF crystallization and washing, potentially leading to rapid COF development and scale up. In an attempt to capture sample to sample variability of this packed-bed reactor approach, the synthesis was performed in duplicate and the variability of the calculated crystallite size was reasonable (Figure 3a, pink).

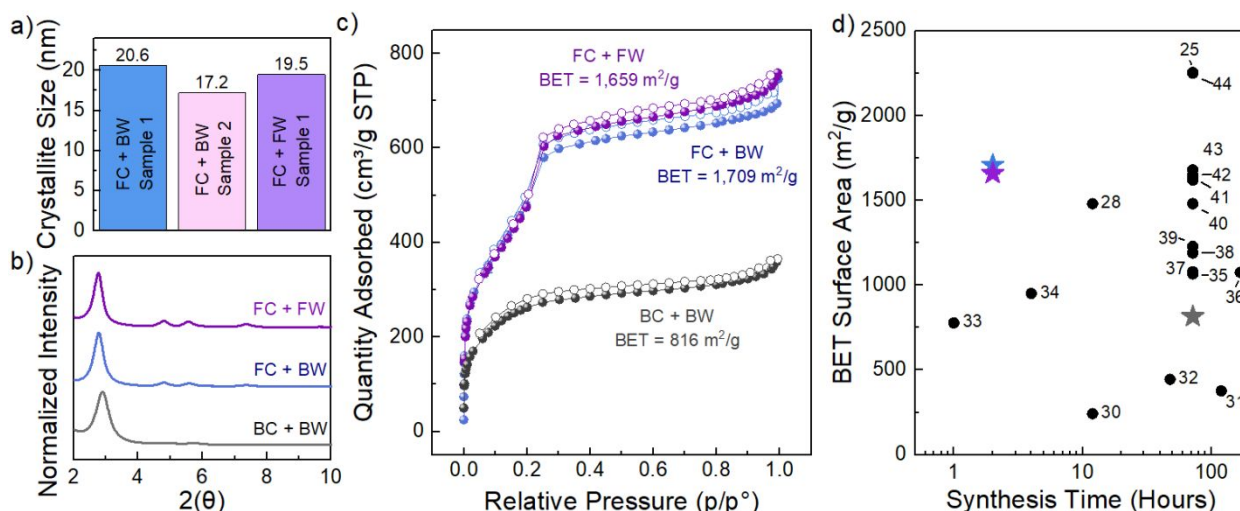


Figure 3. PXRD and Surface Area Comparison of Batch Washing and In Flow Washing a) Crystallite size of flow conversions where FC + BW indicates flow conversion + Batch Wash (140 °C / 2 hours); FC + FW indicates flow conversion + flow wash (140 °C / 2 hours); (b) Normalized PXRD comparison of different combinations of flow and batch methods where BC + BW indicates batch conversion and batch wash (70 °C / 72 hours); (c) respective BET surface area analysis (d) surface area comparison with existing literature (data labels indicate citation number listed in the references).

To further confirm the efficacy of the packed-bed flow method for COF crystallization, BET analysis on the standard batch-washed and flow-washed samples was conducted. For the flow conversion/batch washed sample results indicate a surface area of 1,709 m²/g. This is well above the batch conversion/batch washed method at 70 °C for 72 hours which exhibited a surface area of only 816 m²/g (Figure 3c). Using this new in-line wash-in-flow method a surface area of 1,659 m²/g was achieved. This surface area is nearly identical to batch washing approach but offers the advantage of being able to be implemented in a continuous manufacturing approach, instead of relying on traditional human performed decanting steps. With respect to other synthetic procedures for TAPB- OHPDA COF powders (Figure 3d),^{25,28,30–44} the results from this work clearly show that the implementation of flow chemistry allows for rapid conversion to crystalline material, reducing the standard 72-hour synthesis time by more than 36x for the same quality, or better. To further demonstrate generalizability, this method was extended to the synthesis of TAPB-PDA COF, which is derived from 1,3,5-tris(4-aminophenyl)benzene and terephthalaldehyde (PDA). After synthesis of the amorphous polymer, PXRD results confirm that our packed-bed flow chemistry approach can also produce highly crystalline TAPB-PDA COF powders (further details in Figure S10). Overall, COF powders rapidly crystallized in packed-bed flow reactors present an opportunity to significantly speed up growth and reduce processing times required for high quality materials. The flow processing component also allows for this method to be applied on a larger scale.^{45,46} The amount of COF crystallized in this setup could be increased by simply using a fixed-bed reactor with a larger volume. Furthermore, the flow set-up used in this study could be altered to implement an analogous film synthesis by placing an in-line flow cell with a substrate to perform top-down assembly of COF particles directly onto a surface.^{23,24} The mixing of reagents under continuous flow conditions allows for higher surface area-to-volume ratios²² and fine control of the crystallization and

resulting nanostructure,^{20,34,47} which can aid in fine-tuning the required synthetic steps for future unexplored COF systems.

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Conflicts of interests

There are no conflicts to declare.

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