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ARTICLE

Enhancement of Crystallinity of Imine-linked Covalent Organic Frameworks via Aldehyde Modulators

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Organic additives known as modulators have been used to improve the crystallinity of covalent organic frameworks (COFs) and metal-organic frameworks (MOFs). Here, we demonstrate that benzaldehyde is an effective modulator for enhancing the crystallinity and porosity of imine-linked covalent-organic frameworks (COFs). We varied the amount of benzaldehyde added during COF synthesis and found increased crystallinity and surface areas through powder X-ray dif-fraction (PXRD) and nitrogen gas adsorption measurements, respectively. The improved crystallinity and increased surface area were attributed to the reduced kinetics for COF nucleation and growth, which produced more ordered and crystalline COF materials. This work provides a simple, efficient and general way to improve the crystallinity and porosity of imine-linked COFs and furthers understanding of the role of modulators in the synthesis of COFs.

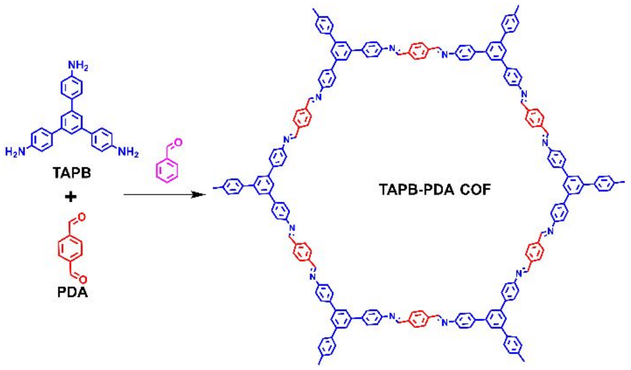
Introduction

Covalent Organic Frameworks (COFs) are highly porous, crystalline organic materials with regular pore structures, tunable functionalities, and high surface areas[1]. These materials have enormous potential for applications including contaminant adsorption[2], membrane separation[3], and catalysis[4]. COFs with a polyimine structure are particularly promising for applications because they generally show excellent stability to a variety of environments[5]. For example, unlike boroxine-linked COFs, imine-linked COFs are stable in aqueous media[5].

However, the synthesis of well-defined, highly crystalline COFs remains a significant challenge[6]. Typically, COFs are synthesized via dynamic, reversible chemistries, and the crystallinity of the resulting material is sensitive to a variety of reaction conditions[7]. Imine-linked COFs are formed through the dynamic and reversible reaction between multi-functional amine and multi-functional aldehyde monomers. The reaction first produces an amorphous network which can re-arrange over time to produce an ordered, crystalline and porous COF[7]. Therefore, the final COF material usually contains a mixture of crystalline and amorphous regions.

To improve the crystallinity of imine-linked COFs, a number of approaches have been implemented. These include modifying the structure of COFs to include hydrogen bonding interactions which can increase the strength of interlayer interactions[8,9] and incorporating fluorine atoms which produce self-complementary π-electronic interactions and increase the total crystal stacking energy and minimizing the unit cell size[10]. However, these methods are limited to specific COF chemistries.

Organic additives known as modulators can improve COF crystallinity by slowing down the crystal nucleation rate and preventing the rapid growth of amorphous precipitates[6]. These modulators are mono-functionalized terminating ligands that can compete with the multi-functional bridging monomers during COF growth. For example, aniline facilitates the formation of large, three-dimensional imine-linked COF single crystals[6], and by controlling the aniline concentration, the size of COFs can be rationally tuned. Bein et al.[11] also enhanced COF crystallinity using a mono-functional boronic acid modulator. They incorporated thiol and carboxylic acid functional groups in the modulator, which were integrated into the COF structure and provided options for further synthetic modifications. Castano et al.[12] studied the nucleation kinetics in the presence of 4-tert-butylcatechol as a competitor in boronate ester-linked COFs and discovered that the competitor could effectively suppress colloid nucleation, enabling anisotropic growth of COFs at high monomer concentrations. Wang et al.[13]



Scheme 1. Reaction scheme for the preparation of TAPB-PDA COFs in the presence of benzaldehyde

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x and Liu et al.[14] controlled the morphology of imine COFs through the use of aniline and/or aldehyde modulators. Wang et al.[13] employed a combination of aniline and benzaldehyde in the polycondensation of 1,3,5-benzenetricarbaldehyde (BTCA) and 1,3,5-tris(4- aminophenyl) benzene (TAPB), turning the resulting morphology to microspheres, fibers or flakes.

In the study described herein, we were interested in studying benzaldehyde as a modulator for COF growth. Benzaldehyde has not been reported as a modulator on its own, and as a simple, cheap, and readily available small molecule, it represents perhaps the simplest aldehyde modulator to use for COF synthesis. Furthermore, prior studies with boronic ester linked COFs found that thiol-functionalized modulators can be used to change the surface chemistry of the final material and place thiol functional groups on the COF surface[11]. We were interested in understanding whether benzaldehyde could be effectively be used to improve crystallinity and porosity without changing the chemistry or morphology of the final COF material. Since benzaldehyde functional groups are present in many building blocks for imine-linked COFs, we reasoned that it would be displaced during COF growth and crystallization. Finally, we were motivated to expand the variety and understanding of modulators for COF synthesis. Modulators have been extensively applied to the synthesis of metal-organic frameworks (MOFs)[15–17] to control growth and improve crystallinity of the final products. Additionally, modulators can be used to control the morphology[18,19], colloidal stability and polydispersity[20], defect structure[21] and crystallinity of MOFs[22]. By comparison, the development of modulators for COFs remains limited. Additional studies and development of modulators can help improve the quality and accessibility of COF materials.

Herein, we first report the separate use of benzaldehyde as a novel modulator for the synthesis of imine-linked COFs. Wang et al.[13] once adapted the combination of aniline and benzaldehyde as the modulators, however, it is hard to exclude the modulation effect of aniline or the imine monomer generated from reaction of aniline and benzaldehyde, and thus it is hard to identify whether separate addition of benzaldehyde can also serve as effective modulator. We hypothesized that benzaldehyde would compete with multi-functional aldehydes during reaction, slow down the COF nucleation rate, and produce COFs with improved crystallinity and higher surface areas.

Results and Discussion

To test our hypothesis, we first studied benzaldehyde as a modulator for the reaction between 1,3,5-tris(4-aminophenyl)benzene (TAPB) and terephthalaldehyde (PDA) to generate TAPB-PDA COF (see Scheme 1). We chose this COF because it has been widely studied, including through studies that provided mechanistic insights of COF formation[7]. With the well-established formation mechanism of TAPB-PDA COF, we could focus more on the reaction process involving benzaldehyde. We added benzaldehyde to stoichiometric amounts of TAPB and PDA, which were dissolved in a 2 mL mixture of dioxane and mesitylene (v/v: 4/1) along with 0.2 mL 6M acetic acid as the catalyst. All reactions were conducted at 120 ˚C for 24 hours, after which samples were collected and washed for further analysis (see details in ESI†). The amount of benzaldehyde added was designed to range from 0 to 9 equivalents relative to TAPB.

An insoluble powder was formed in all cases, and a combination of Fourier-transform infrared spectroscopy (FTIR), solid state ^{13}C CP-MAS NMR spectroscopy, and powder X-ray diffraction (PXRD) measurements confirmed successful polycondensation of TAPB and PDA to form the target TAPB-PDA COF. Under FTIR analysis, a C=N stretching vibration band at 1619 cm^{-1} appeared and the aldehyde band at 1681 cm^{-1} was attenuated after the reaction, indicating the formation of imine bonds (Fig. S1-S2, ESI†). Solid state ^{13}C cross polarized magic angle spinning (CPMAS) NMR revealed imine linkage formation reflected in a characteristic resonance signal around 158 ppm[23](Fig. S6, ESI†).

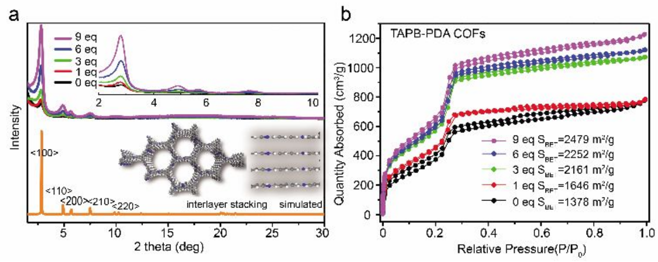


Fig. 1 (a) (top) Experimental PXRD traces of TAPB-PDA COF produced in the presence of varying amounts of benzaldehyde, from 0 to 9 eq. relative to TAPB monomer. (bottom) Simulated diffraction spectra and predicted molecular structure. (b) Nitrogen adsorption and desorption isotherms (77 K) of TAPB-PDA COFs synthesized with different equivalents of benzaldehyde added (black: 0 eq; red: 1 eq; green: 3 eq; blue: 6 eq; magenta: 9 eq).

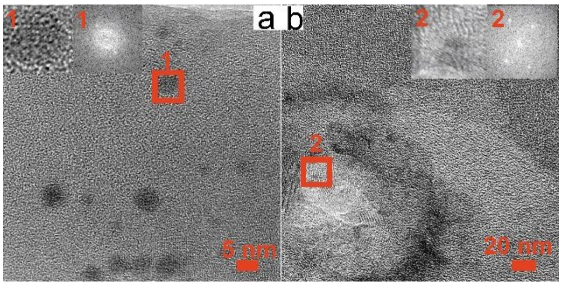


Fig. 2 HRTEM micrographs of TAPB-PDA COF, (a) synthesized without benzaldehyde, (b) synthesized with 9 eq. benzaldehyde added. Insets show four regions of interest at higher magnification along with the FFT of each region (the predominant diffraction features correspond to a d-spacing of approximately 30 Å).

Analysis by powder X-ray diffraction (PXRD) revealed spectra consistent with prior reports on TAPB-PDA COF[7]. The diffraction peak at 2.88˚ corresponds to the <100> reflection, while the peaks at 5˚, 5.7˚, 7.5˚, and 10˚ were assigned to <110>, <200>, <210>, and <220> hexagonal reflections, respectively (Lattice parameters and atom coordinates are given in ESI†). A minor peak at 25˚ was also observed and attributed to the 0.36 nm interlayer stacking of the imine-linked 2D sheets[7]. Besides, all these PXRD spectra are in good agreement with the simulated diffractions of AA stacking. An increase of crystallinity with increasing amount of benzaldehyde modulator was clearly observed from PXRD spectra, as shown in Fig. 1. All PXRD analyses were performed using the same testing conditions and similar amount of powders levelled flat on a zero-background substrate. With increasing amounts of benzaldehyde modulator, the <100> peak at 2.88˚ sharpens and increases in peak intensity. Also, the full width at half maxima (FWHM, see table S1) of the PXRD peak 2θ = 2.88° decreases with increasing benzaldehyde content.

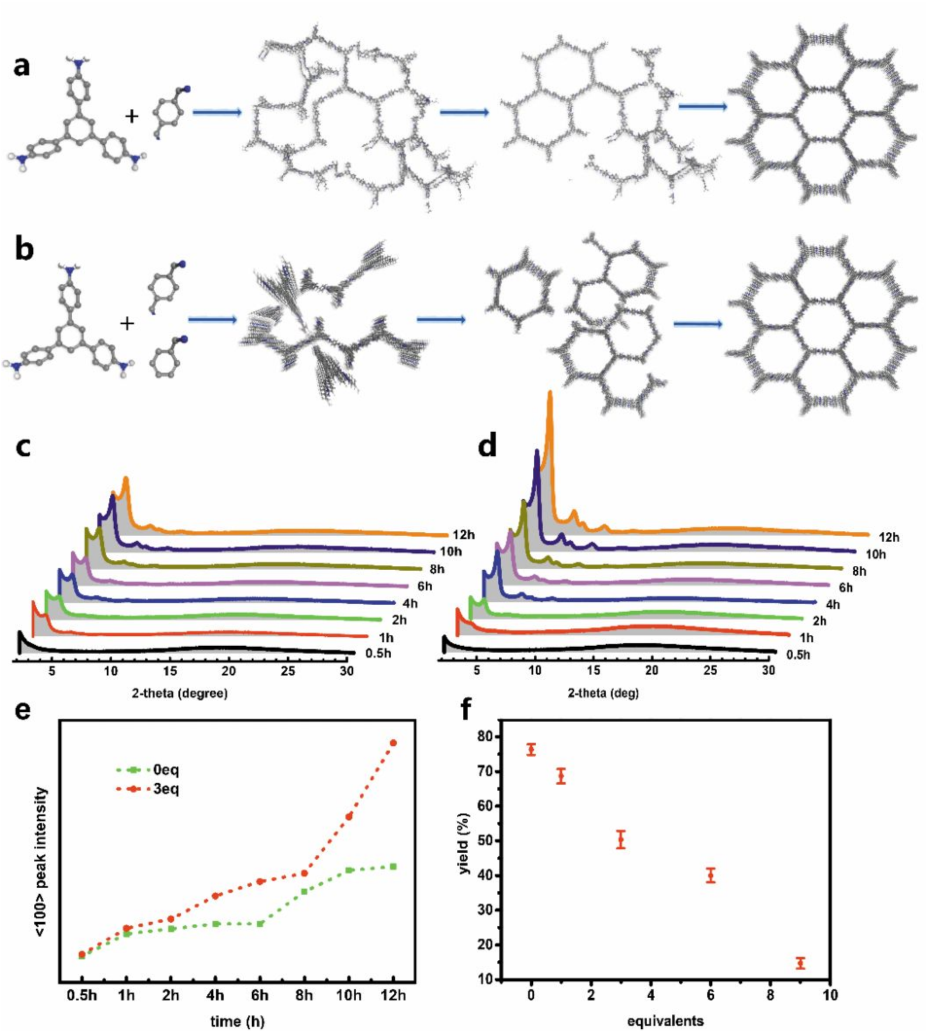


Fig. 3 Schematics for the formation of imine TAPB-PDA COFs (a) without benzaldehyde added and (b) with benzaldehyde added. Time-dependent PXRD measurements of TAPB-PDA COFs at different reaction at different times (c) without benzaldehyde added and(d) with 3 eq benzaldehyde added. (e) Comparison of <100> PXRD peak intensity of TAPB-PDA COFs synthesized with 3 eq or without benzaldehyde and (f) isolated yields of TAPB-PDA COF powders with different equivalents of benzaldehyde added.

Improved crystallinity of porous materials is generally correlated with a more ordered structure and higher surface areas[10]. To test this in the TAPB-PDA COFs formed in the presence of benzaldehyde, nitrogen sorption isotherm measurements were acquired at 77 K (see Fig.2 and Fig. S8, ESI†) and surface areas were calculated using the Brunauer–Emmett–Teller (BET) model. Significant increases of surface areas were observed with the addition of benzaldehyde. TAPB-PDA COFs synthesized without benzaldehyde had a total surface area of 1378 m^2/g, while COFs synthesized with 9 eq benzaldehyde had a surface area as high as 2480 m^2/g.

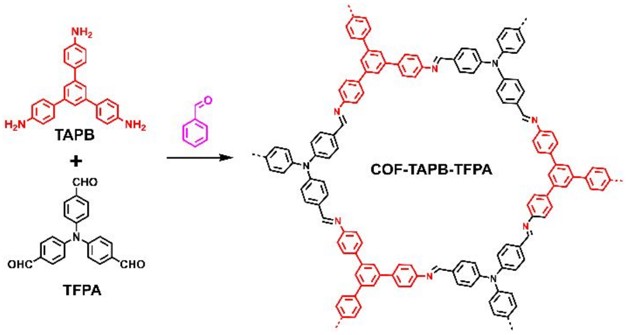
We also used high-resolution transmission electron microscopy (HRTEM) to visualize crystalline domains. We analysed COF samples synthesized without benzaldehyde (Fig. 2a) or with 9 eq benzaldehyde (Fig. 2b). Both exhibited crystalline regions with lattice fringes, as reflected in the inset images of selected regions of the sample. FFT analysis reveals hexagonal packing with lattice spacings of approximately 30 Å, which is consistent with the d_{100} spacing values determined by PXRD. The HRTEM micrographs also reveal amorphous sample regions, which can be attributed in part to beam damage during HRTEM analysis.

As expected, benzaldehyde modulator did not change the chemistry or structure of COFs except the enhancement of crystallinity and surface areas. This is evidenced by the identical ^{13}C CP-MAS NMR and FTIR spectra (Fig.S1-2, S6) regardless of the amount of benzaldehyde added. Unlike the other modulators used in imine-COFs that alternate their morphology[13,14] and particle size[6], benzaldehyde did not change the morphology and particle size of these polycrystalline COFs as evidenced by scanning electron microscopy (SEM, Fig. S10, ESI†), which can be very useful in some cases when we do not expect a morphology change. Furthermore, thermogravimetric analysis (TGA) measurements (Fig. S12, ESI†).

under an argon atmosphere exhibiting similar decomposing temperature, proved that benzaldehyde does not alternate the thermal stability of COFs.

Similar to other modulators reported[6,11,13,14], we propose a mechanism that benzaldehyde decreases the rate of COF growth and increases the formation of crystalline domains over amorphous COF domains. This is shown schematically in Figs. 3a and b. In the absence of benzaldehyde modulator, the amine and aldehyde monomers react quickly to first form an amorphous covalent framework, followed by improved crystallinity through slow rearrangement of the framework bonds. In the presence of benzaldehyde, amine monomers will first react with both multi-functional PDA and mono-functional benzaldehyde, producing a larger quantity of oligomers since benzaldehyde end-caps growth. These smaller oligomers will then continue to react via imine exchange and more efficiently reorganize to form ordered, crystalline COF domains.

Consistent with this mechanism, aliquots taken over time indicate that the crystallinity improves with time both with and without benzaldehyde but is always higher for samples synthesized with benzaldehyde modulator (see Figs. 3 c - e). Furthermore, without benzaldehyde, we observed insoluble powders precipitated out immediately upon addition of acetic acid catalyst, while with 9 eq benzaldehyde, the solution became cloudy after 30 minutes. We attributed this phenomenon to the more soluble oligomers formed initially with existence of benzaldehyde. Furthermore, the yields of COF products were also observed to decrease dramatically with increasing benzaldehyde added (Fig. 3f), which is consistent with reports from Wang et al.[13]. This could also be ascribed to the increasing amount of more soluble oligomers generated by TAPB and benzaldehyde. Those more soluble oligomers were washed away during centrifugation and filtration, thus the amount of insoluble powders finally obtained decreased significantly. Despite the trade-off between crystallinity and yield, the <100> peak intensity of TAPB-PDA COFs synthesized with 3 eq benzaldehyde was almost twice over that without benzaldehyde (Fig.3e) after 12 reaction hours, but the yield did not deceased a lot compared to that without benzaldehyde. Hence, the crystallinity can be tuned and enhanced with addition of moderate amount of benzaldehyde without significantly decreasing their yields. Finally, time-dependent FTIR spectra do not show any chemical changes in the COF structure after 30 minutes of reaction time (Fig.S3, ESI†), which suggests that the reaction only involves network/bond rearrangement and not a change in COF chemistry.



Scheme 2 Reaction scheme for the preparation of TAPB-TFPA COFs in the presence of benzaldehyde

To test the generality of using benzaldehyde as a modulator, we studied the formation of a different imine COF, TAPB-TFPA COF[24], in the presence of benzaldehyde, as shown in Scheme 2. We varied the benzaldehyde content from 0 – 4 eq. and compared the PXRD patterns with and without benzaldehyde introduced. One important aspect worth mentioning is that the PXRD patterns of these COFs are identical with that in previous report by Jiang et al[24]. Similar to their reports, we could not elucidate the peak around 5.3°, but all other peaks are in good agreement with simulated XRD patterns of AA stacking. As shown in Fig. 4a, the crystallinity increases with benzaldehyde, and the sharpest diffraction peaks are observed for the sample with 4 eq. benzaldehyde. Furthermore, nitrogen adsorption measurements (see Fig. 4b, Fig S9) show COFs have larger surface areas with greater amounts of benzaldehyde. We also observed that addition of 4 eq. of benzaldehyde made both the peak intensity at 4.8° and the BET areas were almost three times as large as that without benzaldehyde. However, the yield only decreased from 86.9% to 50.6%. FT- IR (Fig. S4 and S5, ESI†) and solid state ^{13}C NMR spectroscopy (Fig. S7, ESI†) confirm the successful formation of imine linkages and show that benzaldehyde does not change the chemistry of the final COF materials. SEM (Fig. S11, ESI†) and TGA analysis (Fig. S13, ESI†) show similar morphology and thermal stability across the series of samples. Overall, these results indicate that benzaldehyde can enhance the crystallinity of imine-linked COFs without changing their chemistry and morphology.

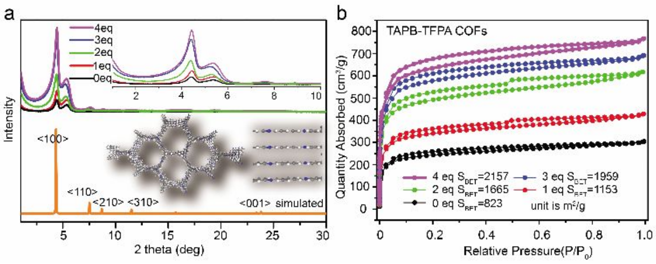


Fig. 4 (a) (top) Experimental PXRD patterns of TAPB-TFPA COF produced in the presence of varying amounts of benzaldehyde, from 0 to 4 eq. relative to TAPB monomer. (bottom) Simulated diffraction spectra and predicted molecular structure. **(b)** Nitrogen adsorption and desorption isotherms (77 K) of TAPB-TFPA COFs synthesized with different equivalents of benzaldehyde added (black: 0 eq; red: 1 eq; green: 2 eq; blue: 3 eq; magenta: 4 eq).

Conclusion

In summary, this study shows that benzaldehyde is a simple and effective modulator to improve the crystallinity of imine-based COFs. The simple structure of benzaldehyde without any functional groups will not alternate the chemistry of COFs. And with addition of 3~4 eq. benzaldehyde, the crystallinity and BET surface areas of COFs was largely enhanced, while the yield did not decrease significantly. Time-dependent PXRD and FTIR measurements along with yield comparison revealed the formation mechanism of more highly ordered COFs produced in the presence of benzaldehyde. We anticipate this simple approach will broaden the ways to obtain high-quality crystalline COFs for applications including catalysis, gas adsorption, and gas storage.

Acknowledgments

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Conflicts of interest

There are no conflicts to declare.

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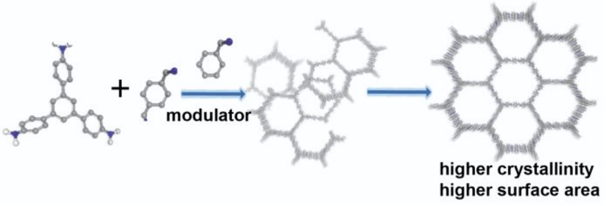

Benzaldehyde is found to be an effective modulator for enhancing the crystallinity and porosity of imine-linked covalent-organic frameworks (COFs).