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Switching On and Off Interlayer Correlations and Porosity in 2D Covalent Organic Frameworks

Torben Sick,¹ Julian M. Rotter,¹ Stephan Reuter,¹ Sharath Kandambeth,¹ Nicolai N. Bach,¹ Markus Döblinger,¹ Julia Merz,² Timothy Clark,³ Todd B. Marder,² Thomas Bein^{1*} and Dana D. Medina^{1*}

¹ Department of Chemistry and Center for NanoScience (CeNS), University of Munich (LMU), Butenandtstraße 5-13, 81377 Munich, Germany

² Institute für Anorganische Chemie and Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

³ Computer-Chemistry-Center, Department of Chemistry and Pharmacy, Friedrich-Alexander-University Erlangen-Nuremberg, Naegelsbachstr. 25, 91052 Erlangen, Germany.

Covalent Organic Frameworks, COFs, porous polymers, dynamic structure, porosity, crystallinity, supercritical carbon dioxide, scCO₂, benzodithiophene

ABSTRACT: Two-dimensional covalent organic frameworks (2D COFs) attract great interest owing to their well-defined pore structure, thermal stability, high surface area and permanent porosity. In combination with a tunable chemical pore environment, COFs are intriguing candidates for molecular sieving based on selective host-guest interactions. Herein, we report on 2D COF structures capable of reversibly switching between a highly correlated crystalline, porous and a poorly correlated, non-porous state by exposure to external stimuli. To identify COF structures with such dynamic response, we systematically studied the structural properties of a family of two-dimensional imine COFs comprising tris(4-aminophenyl)benzene (TAPB) and a variety of dialdehyde linear building blocks including terephthalaldehyde (TA) and dialdehydes of thienothiophene (TT), benzodithiophene (BDT), dimethoxybenzodithiophene (BDT-OMe), diethoxybenzodithiophene (BDT-OEt), dipropoxybenzodithiophene (BDT-OPr) and pyrene (Pyrene-2,7). TAPB-COFs consisting of linear building blocks with enlarged π -systems or alkoxy functionalities showed significant stability towards exposure to external stimuli such as solvents or solvent vapors. In contrast, TAPB-COFs containing unsubstituted linear building blocks instantly responded to exposure to these external stimuli by a drastic reduction in COF layer correlation, long-range order and porosity. To reverse the process we developed an activation procedure in supercritical carbon dioxide (scCO₂) as a highly efficient means to revert fragile non-porous and amorphous COF polymers into highly crystalline and open porous frameworks. Strikingly, the framework structure of TAPB-COFs respond dynamically to such chemical stimuli, demonstrating that their porosity and crystallinity can be reversibly controlled by alternating steps of solvent stimuli and scCO₂ activation.

INTRODUCTION

Covalent organic frameworks (COFs) are a class of organic crystalline porous materials obtained by connecting organic building blocks through covalent bonds.¹ The dynamic nature of the bonds formed, in classes of compounds comprising mainly boroxines,²⁻³ boronic esters,⁴⁻⁹ imines,¹⁰⁻¹³ azines,¹⁴⁻¹⁵ imides,¹⁶⁻¹⁷ hydrazones¹⁸⁻²⁰ and triazines,²¹⁻²⁴ and the defined geometries of the COF building blocks are two essential conditions for attaining ordered framework structures.²⁵⁻²⁶ In two-dimensional COF materials (2D COFs), extended molecular sheets interact through weak attractive forces to form defined molecular stacks and open porous channels. Therefore, the π -stacking interactions between adjacent COF layers play a pivotal role in achieving accessible surface area, and structural stability.²

In recent years 2D COFs have been examined in the context of applications related to functional interfaces capable of specific molecular uptake. Due to their well-defined pore channel structure, sufficiently large pore apertures and tailored pore chemical environment the selective adsorption of molecular agents such as pollutants,²⁷⁻²⁸ chiral compounds²⁹ and chemicals valuable for green chemistry reactions^{5, 30-33} was realized for 2D COF powders and active membranes. Control over the pore chemical environment in principle enables the permeability of these porous frameworks to be tuned to the desired task. This is achieved mainly by installing anchor functional groups providing favorable interactions with the guest molecules. Upon the adsorption of the desired guest molecules, the crystallinity and the integrity of the pore system are expected to be maintained, which can be beneficial for the reverse process of desorption, thereby allowing for cycling of the process.

Another way for modulating the framework's permeability is to control the pore accessibility, namely triggering a switch between an open and a closed pore state by exposure to external stimuli. For example, such a responsive 2D COF platform can be realized by switching between a crystalline, porous and an amorphous, non-porous COF phase in the solid state. As described above, a crystalline 2D COF phase forms via the self-assembly of individual COF layers into well-defined molecular stacks vielding uniform pore shapes, whereas an amorphous phase can be envisioned as COF layers that are randomly shifted in-plane with respect to the adjacent layers, yielding irregular pores and limited or no pore accessibility. Switching between these two states implies that the stacking interactions can be modulated in a 2D COF, namely dynamically tightening and weakening them under specific conditions.

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Crystalline 2D COFs with weak π -stacking interactions are prone to exfoliation into individual layers upon exposure to different solvents and solvent mixtures during sonication^{19, 34-36} or by mechanical exfoliation.³⁷⁻³⁸ The reason for the exfoliation in solution is still to be revealed, nevertheless it is believed that an intercalation of solvent molecules might be the trigger.¹⁹ COFs featuring enhanced π -stacking interactions were reported to be highly stable towards treatments such as post-synthetic solvent immersion. Robust 2D COFs are usually constructed by reinforcing the π -stacking interactions between the COF layers, by methods such as intra-molecular hydrogen bonding, alkoxy group incorporation,³⁹⁻⁴⁰ defined docking of propeller moieties⁴¹ and armchair building ² or by controlling dipolar interactions between COF blocks. layers.⁴³ Jiang and coworkers introduced a strategy to use arene/perfluoroarene-subunits to influence adjacent layers' multipole moments, yielding highly crystalline, alternatingly stacked frameworks.⁴⁴ These methods are aimed at producing structures that maintain their key properties, namely crystallinity and pore integrity, under harsh conditions such as at extreme pH. Therefore, they are suitable for applications requiring defined backbones and stability in a range of chemical conditions.⁴⁵⁻⁴⁸ The realization of a reversible activation and deactivation protocol, switching between two structurally different COF modes in the solid state, is an important fundamental aspect contributing to the understanding of COF framework assembly and allows for control over structural features. To date, reversible switching of crystallinity or porosity in the solid state has been shown only for a very limited number of framework materials. In molecular superstructures⁴⁹ or cages⁵⁰⁻⁵¹ it was possible to switch repetitively at least one of those key materials properties back and forth, mainly due to conformational flexibility in the soft organic material and uptake of guest molecules. In a recent pioneering study, the concept of reversible crystallinity was demonstrated by including guest molecules into a non-crystalline floppy 2D polymer constructed via urea-linkages.⁵² However, to the best of our knowledge, a dynamic switch of both crystallinity and porosity in 'rigid' 2D materials by the exclusion of guest molecules in the solid state is yet to be reported.

Herein, we report the synthesis of a series of hexagonal-pore 2D COFs featuring different levels of structural robustness. In the context of responsive interfaces, their dynamic behavior towards chemical guests such as solvent molecules in the liquid and vapor phases are presented. The COFs were synthesized via an acetic acid-catalyzed Schiff-base condensation reaction of 1,3,5-tris(4-aminophenyl)benzene (TAPB) as a

multidentate building block with a variety of linear dialdehydes. Using unsubstituted linear dialdehydes, namely tereph-(TA), thalaldehvde thieno[3,2-b]thiophene-2,5dicarboxaldehyde (TT) and benzo[1,2-b:4,5-b']dithiophene-2,6-dicarboxaldehyde (BDT) resulted in imine COFs with moderate crystallinity, limited pore accessibility and moderate structural stability towards a variety of external stimuli. These COFs were therefore classified as 'fragile'. COFs featuring a higher degree of structural robustness were obtained by employing BDT cores decorated with alkoxy side groups as building blocks, such as 4,8-dimethoxybenzo[1,2-b:4,5b']dithiophene-2,6-dicarbaldehyde (BDT-OMe), 4.8diethoxybenzo[1,2-b:4,5-b']dithiophene-2,6-dicarbaldehyde (BDT-OEt) and 4,8-dipropoxybenzo[1,2-b:4,5-b']dithiophene-2,6-dicarbaldehyde (BDT-OPr). Alternatively, structural robustness was also achieved by a significant enlargement of the dialdehyde's π -system using pyrene-2,7-dicarboxaldehyde (Pyrene-2,7). In contrast to the fragile COFs, these frameworks display long-range structural order and high surface area even after long exposure to organic solvents and solvent vapors.

Furthermore, we developed a fast, simple and efficient activation protocol using supercritical carbon dioxide (scCO₂) to transform poorly crystalline and moderately porous TAPB-COFs into highly crystalline and open porous frameworks. The scCO₂-activated crystalline and porous fragile COFs were still found to be highly sensitive towards a large variety of organic solvents and vapors. In contrast, the scCO₂-activated robust COFs showed stability towards external stimuli except for 1,4-dioxane exposure. Depending on the fragility of the COF, a significant reduction in long-range order and porosity was recorded upon brief immersion of the COFs in solvents (e.g. rinsing with 1,4-dioxane) or exposure to vapor atmospheres. Remarkably, alternating scCO₂ activation and solvent vapor exposure cycles allowed us to turn on and off the COF's crystallinity and porosity reversibly.

RESULTS AND DISCUSSION

To identify COFs featuring a dynamic response towards external stimuli we focused our study on COFs comprising TAPB building blocks. Those TAPB-COFs were reported to exhibit excellent structural properties such as long-range order, tunable structural properties and high surface areas.^{16, 40, 47,} ⁵³⁻⁶² To explore the stability and crystallinity of TAPB-based frameworks, we synthesized a family of TAPB-COFs with linear counterparts featuring π -systems of different extensions such as TA, TT, BDT and Pyrene-2,7. In addition, we synthesized TAPB-COFs of substituted BDT cores exhibiting different alkoxy side chain lengths, namely BDT-OMe, BDT-OEt, and BDT-OPr. The series of these imine-linked TAPB-COFs was synthesized under solvothermal conditions. Briefly, 1 equiv. of TAPB (0.02 to 0.06 mmol) and 1.5 equiv. of linear dialdehyde (0.03 to 0.09 mmol) were suspended in a mixture of 1,4-dioxane and mesitylene (1.0 mL, 8:1 v:v) in a 6 mL glass tube under argon. The reaction mixture was sonicated for 2 min to obtain a finely dispersed suspension of precursors. After addition of acetic acid as catalyst (100 µL, 6 M) the reaction tube was sealed and placed in a preheated oven at 100 °C for 72 h. The as-synthesized precipitates were isolated by filtration under reduced pressure. Interestingly, powder X-ray diffraction (PXRD) analysis of the as-synthesized, filtered powders revealed moderate to poor crystallinity for all of the examined precipitates (Figures S3-S5). To improve the struc-

tural features, with regard to crystallinity and porosity, of the obtained COFs, namely their long-range order, different isolation and purification procedures were employed. Attempts at removing residual monomers, catalyst agents and solvents solely by vacuum drying and heat activation did not lead to the desired improvement in crystallinity. Surprisingly, employing solvent rinsing of the COF powders with the main reaction solvent, namely 1,4-dioxane, resulted in amorphous powders (Figure S2).



Figure 1. a) Schematic representation of 2D imine COF synthesis from TAPB and a variety of linear building blocks. b)-h) Comparison of the experimental (red) and refined simulated PXRD patterns (black) in conjunction with the difference plot (blue) for the different TAPB-COFs.

Further solvent stability screenings were carried out to identify the optimal conditions for a suitable recovery of crystalline products by a post-synthetic solvent treatment. We chose common commercially available solvents with a polarity gradient ranging from water to toluene and submersed the COF powders for 24 h (5 mg/mL) in the respective solvent to obtain a mild solvent exchange process. We observed a relationship between the extension of the π -system of the linear building block and the structural stability of the COFs. The TA TAPB-COF, comprising a linear building block with comparably small π -system, showed instability towards all the employed solvents, whereas the TT and BDT TAPB-COFs showed a certain degree of stability towards toluene and ethanol, respectively (Figure S4). Nevertheless, the general stability observed towards solvent exchange for all three COFs was moderate (Figures S3a and S4). Investigation of the accessible porosity of TT and BDT TAPB-COFs revealed non-porous or moderately porous frameworks, respectively (Figure S44). Therefore, these unsubstituted COF structures were classified as "fragile" (Figure 1). In contrast, the alkoxy substituted COFs BDT-OMe, BDT-OEt and BDT-OPr TAPB-COFs as well as the Pyrene-2,7 TAPB-COF were found to be highly stable towards the solvent exchange treatment with acetone, ethanol, and toluene. Furthermore, these COFs could even be Soxhlet extracted with toluene, and they exhibited substantially higher crystallinity compared to the as-synthesized powders, indicating a sufficient elution of residual agents along with retention of the structures (Figures S3b and S5). These findings are in accordance with the substantial open porous character of these TAPB-COFs (Figures 2 and S42), which thereby were classified as "robust" (Figure 1).

In the search for a general isolation method that is suitable for both fragile and robust TAPB-COFs, we employed a supercritical fluid activation method using supercritical carbon dioxide. In principle, the supercritical fluid activation is based on the effect of a liquid-like substance above its critical point on a target material. Above the critical point, the liquid-like matter exhibits very low surface tension and thereby capillary forces acting on the walls of the extracted material are significantly reduced. This activation procedure is well established for obtaining highly porous materials⁶³⁻⁶⁷ and was already reported to be useful for the recovery of COFs.^{52, 57, 62, 68-70} In a typical scCO₂ activation process employed in our work, freshly filtered COF powders exhibiting low to moderate crystallinity were transferred to a metal holder and placed in an autoclave, which was then tightly closed and cooled to 5 °C. Subsequently, CO2 was flushed through the system and finally the closed autoclave was heated to 40 °C, while adjusting the pressure to 85 bar to establish supercritical CO₂ conditions (see experimental section for further details). After 2 h, the pressure was slowly reduced and the $scCO_2$ -activated powders were recovered.

Structural Characterization. The crystallinity of scCO₂activated fragile and robust COF samples was investigated by PXRD (Figure 1). Strikingly, for all the COF structures studied, a very intense and sharp reflection at low 20 values corresponding to the 100 crystal plane was observed, indicating highly crystalline materials. For the TA and TT TAPB-COFs, this reflection appears at $2\theta = 2.53^\circ$, d = 34.9 Å and $2\theta =$ 2.73° , d = 32.3 Å, respectively. The unsubstituted and substituted BDT TAPB-COFs (BDT TAPB-COF, BDT-OMe TAPB-COF, BDT-OEt TAPB-COF, BDT-OPr TAPB-COF) exhibit the 100 reflection at $2\theta = 2.30^{\circ}$, corresponding to a dspacing of 38.4 Å. For the Pyrene-2,7 TAPB-COF, the 100 reflection appears at $2\theta = 2.28^\circ$, corresponding to the largest unit cell of the TAPB-COF series with a d-spacing of 38.7 Å. The intense 100 reflection is followed by weaker, higher order reflections that are attributed to the 110, 200, 210, 220, 230, 310, and 001 planes. We modeled the COF structures in the P6 space group, corresponding to a fully overlapped AAeclipsed stacking model. The unit cell parameters of the COFs were determined by performing Pawley refinements with respect to the experimental diffraction patterns (Figure 1). The comparison between the experimental and the simulated PXRD patterns shows close matching for all reflection positions (Figure 1b-g). The d-spacings corresponding to the broad 001 reflections positioned at $2\theta = 24-27^{\circ}$ with maxima at ca. $2\theta = 25.1^{\circ}$ were calculated to be ca. 3.55 Å and are attributed to the COF's interlayer distances. As an exception, Pyrene-2,7 TAPB-COF exhibits a 001 reflection at $2\theta = 25.7^{\circ}$ corresponding to a comparably closer stacking distance of adjacent layers of 3.46 Å. In a previous report, the TAPB was shown to be a key factor for obtaining highly crystalline frameworks attributed to its inherent propeller structure induced by steric constraints.⁴¹ Thereby, the TAPB allows for spatial control and a precise arrangement of adjacent layers by influencing the interlayer distance. Herein, we reveal that the interlayer distances can be controlled by the nature of the linear counterparts. Using a linear pyrene linker between the TAPB building blocks results in a closer interlayer distance of the adjacent COF-layers, demonstrating that the TAPB propeller has a certain degree of flexibility.

The long-range order established by employing the scCO₂ activation process was monitored over the course of several weeks (Figure S15). The scCO₂-activated fragile and robust TAPB-COFs maintained their highly crystalline character during this time, rendering these COFs stable under ambient conditions, thus exhibiting a significant shelf life.

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Figure 2. Space filling model showing the hexagonal pore channels of (a) the fragile BDT TAPB-, and (b) the robust BDT-OMe TAPB-COF. (c) Schematic representation of the impact of solvent treatment and subsequent vacuum drying on BDT TAPB-COF (left) and BDT-OMe TAPB-COF (right). (d) PXRD of the BDT TAPB-COF upon solvent treatment and subsequent vacuum drying. (e) PXRD of the BDT-OMe TAPB-COF upon solvent treatment and subsequent vacuum drying.

The porosity of the scCO₂-activated fragile and robust COF samples was investigated by nitrogen physisorption. The type IVb isotherms are characteristic for mesoporous materials with pores smaller than 5 nm (Figures S39 – 42).⁷¹ For all scCO₂-activated COFs, high surface areas of up to 2000 m²g⁻¹ were determined, which illustrates the power of the scCO₂ activation as a general method providing highly porous and crystal-line COF materials (for details on BET surface areas, pore volumes and pore size distributions see Table S2 and Figures S39-S43 in the Supporting Information).

Scanning electron micrographs (SEM) of the highly crystalline COF powders revealed either spherical or rod-like COF particle assemblies (Figures S34-S36). Among the different COFs, the TT TAPB-COF forms unique monodispersed spherical particles of ca. 5 μ m (Figure S35c). Furthermore, we investigated the morphological properties of TT TAPB-COF following a previously reported reaction scheme using anisole/ethanol as the solvent mixture.⁴¹ Under these synthesis conditions, the monodisperse TT TAPB-COF particles obtained are 2 μ m in diameter and, in some cases, self-organization into larger spherical hollow superstructures was observed (Figure S36).

Remarkably, structural analysis of the unsubstituted COF powders via transmission electron microscopy (TEM) reveals crystallites with domain sizes of up to 500 nm (Figure S37). Specifically, the Pyrene-2,7 TAPB-COF exhibits well-faceted hexagonally shaped crystals and the BDT TAPB-COF exhibits large domain sizes of up to 500 nm. To illustrate further the impact of scCO₂ activation on structural features, we characterized an as-synthesized and vacuum dried fraction, a 1,4-dioxane treated fraction (24 h exposure to 1,4-dioxane vapor) and a scCO₂-activated fraction of the same sample of BDT TAPB-COF by TEM (Figure S38). The scCO₂-activated BDT TAPB-COF sample shows enlarged crystalline domains of up

to 100 nm (Figure S38c). In contrast, the filtered and vacuum dried and the 1,4-dioxane-rinsed BDT TAPB-COF fractions only exhibit short-range ordered domains of up to 10 nm (Figure S38a and b). Interestingly, the scCO₂-activated robust BDT-COFs show significantly smaller domain sizes of 20-80 nm (Figure S37). This can be attributed to the sterically demanding side chains and electrostatic repulsion caused by the alkoxy chains, which can impact the packing of the COF layers.

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TABP-COF Response Towards Solvent and Vapor Stimuli. After achieving structural stability and permanent porosity under ambient conditions through scCO₂ activation of the TAPB-COFs, their stability towards external solvent stimuli was investigated. To this end, the crystalline and porous scCO₂-activated COF powders were immersed for 24 h in the different solvents of the series described earlier (acetone, ethanol, toluene, water, 1,4-dioxane, 5 mg/mL). Prior to PXRD analysis, the powders were filtered and vacuum dried to remove residual solvent molecules. In the case of the fragile COFs, a pronounced decrease in long-range order was detected (Figure 2). In contrast, the robust TAPB-COFs maintained their crystallinity when exposed to all of the employed solvents excluding water and 1,4-dioxane (Figures S6b and S8). To rule out the possibility of simple decomposition of the fragile COF samples during exposure to solvents, we conducted IR measurements of the scCO2-activated and the 1,4dioxane treated fragile BDT TAPB-COF and the robust BDT-OMe TAPB-COF samples (Figures S32 and S33). All IR spectra of the solvent-treated COFs exhibit vibrational absorption bands comparable to those of the highly porous and crystalline scCO₂-activated samples, hence excluding decomposition or new bond forming processes.

Next, we examined the interactions of the scCO₂-activated crystalline frameworks with different solvent vapors. We anticipated that the vapor treatment would have a smaller impact on the COF structures compared to exposure to liquid solvents. For these experiments, the scCO₂-activated TAPB COF samples were placed, for 24 h, in a closed vapor chamber containing an open reservoir of the respective solvent. The resulting powders were subjected to reduced pressure (10⁻³

mbar) for 30 min to remove residual guest molecules located in the pores prior to PXRD analysis (Figures S9-S11). Surprisingly, the fragile COFs were still affected by the interaction with solvent vapors and suffered a reduction in long-range order demonstrated by the 100 line broadening and relative intensity (Figures S9a and S10). Similar to what was observed upon immersion in solvents, the robust TAPB-COFs maintained their high crystallinity upon the exposure to vapors of acetone, ethanol and toluene. Upon exposure to water and 1,4dioxane vapors, the robust COFs showed high vulnerability (Figures S9b and S11). To investigate the strong impact of solvent vapors on the TAPB-COF structures, time-dependent PXRD measurements were conducted for a fragile and a robust TAPB-COF. As representative model systems, BDT TAPB-COF (fragile) and BDT-OMe TAPB-COF (robust) were selected for these experiments and were exposed to different solvent vapors. We chose 1.4-dioxane and ethanol as solvent vapors, because both frameworks were highly affected by 1,4-dioxane immersion, while ethanol immersion did not lead to complete framework degradation in both cases. For these experiments, highly crystalline scCO₂-activated TAPB-COF powders spread on a silicon wafer were placed in a plastic bag and immobilized on the PXRD measuring stage. An open vessel filled with the respective solvent was included within the plastic bag, which then was tightly closed allowing for a solvent vapor saturated atmosphere inside the bag. Subsequently, PXRD patterns of the COF powders were collected in a continuous cyclic mode with 2.5 min measurement time. In these experiments, we found that exposing both BDT and BDT-OMe TAPB-COF powders to 1,4 dioxane vapor resulted in a poorly crystalline material. This is an interesting observation as 1,4-dioxane is the main solvent in the TAPB-COF bulk syntheses, aiding the progressive construction of the frameworks. The loss of structural order was observed by a steady decrease in the diffraction intensity of the 100 reflections in the course of increasing vapor exposure time. Notably, we did not observe changes in the diffraction reflection positions of the 100 and higher order reflections in the ab-plane during these experiments (Figure 3b).



Figure 3: (a) Schematic representation of the structural transformation of highly ordered COF layers upon vapor treatment with 1,4dioxane to low ordered and non-porous materials and a subsequent supercritical reactivation to highly ordered porous polymers. (b) PXRD and TEM of BDT TAPB-COF after synthesis and activation with $scCO_2$ (left), after exposure to 1,4-dioxane vapor (middle) and after reactivation with $scCO_2$ (right). c) N₂-physisorption isotherms and calculated pore size distributions of BDT TAPB-COF after synthesis and activation with $scCO_2$ (left), after exposure to 1,4-dioxane vapor (middle) and after reactivation with $scCO_2$ (reght). (d) PXRDs of BDT TAPB-COF after (re-)activation in $scCO_2$. (e) PXRDs of BDT TAPB-COF after treatment in 1,4-dioxane vapor. (f) Comparison of the calculated BET surface areas of BDT TAPB-COF after $scCO_2$ (re-)activation (blue) and 1,4-dioxane vapor treatment (red).

The amorphization process can be associated with a random displacement of the COF layers. In contrast to the exposure to 1,4-dioxane, both model systems (fragile BDT TAPB-COF; robust BDT-OMe TAPB-COF) showed a certain degree of tolerance towards exposure to ethanol vapor. Importantly, we detected a pronounced shift of the 001 reflection towards lower 20 values corresponding to an increased stacking distance of the adjacent COF layers upon vapor exposure for both the fragile BDT TAPB-COF as well as the robust BDT-OMe TAPB-COF (Figure S16). In combination with the IR investigations indicating a chemically intact imine polymer layer (Figures S32 and S33), this observation points to a slow aniso-

tropic displacement of the COF layers promoted by the weakening of the stacking interactions, thereby resulting in the loss of most structural features.

As the solvent vapors show a slowly progressing effect on the 001 reflections accompanied by a decrease in all other reflection intensities, we studied the effect on the 001 reflections in further detail for both model systems exposed to a small volume of different solvents. We therefore conducted PXRD measurements with scCO₂-activated TAPB-COF samples being soaked with a droplet of either ethanol, 1,4-dioxane or toluene to examine the immediate impact on the framework's stacking distances. We detected shifts of the 001 reflections towards smaller 20 values (Figure S18–S19). For the fragile BDT TAPB-COF and a droplet of 1,4-dioxane we detected a shift from $2\theta = 25.1$ to 22.7° corresponding to interlayer distances of 3.52 Å and 3.91 Å, respectively. In comparison, the 001 reflections of the robust BDT-OMe TAPB-COF shifted from $2\theta = 25.1$ to 24.2° upon treatment with a droplet of 1,4-dioxane, corresponding to interlayer distances of 3.52 Å and 3.68 Å, respectively. The dynamic character of the layer distance enlargements can also be seen by comparison of the samples being treated with toluene droplets. For the robust BDT-OMe TAPB, the interlayer distance shifted from $2\theta =$ 25.1 to 24.4°, corresponding to interlayer distances of 3.52 Å and 3.64 Å upon exposure to toluene. The stacking distance of BDT TAPB-COF shifted from $2\theta = 25.1$ to 24.7° upon the treatment with a droplet of toluene, corresponding to interlayer distances of 3.52 Å and 3.60 Å, respectively. These results underline the significant effect of solvents on the COF's stacking distance and the amorphization process.

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Switching On and Off Crystallinity and Porosity in TAPB-COFs. Strikingly, by employing a scCO₂ reactivation process for the vapor and solvent treated samples, we were able to retrieve highly crystalline COFs featuring the close stacking distances observed prior to vapor and wetting experiments (Figures S17-19). This indicates that the process of gradual loss of structural order is reversible for all TAPB-COFs and that a poorly-crystalline TAPB-based polymer can be converted back into a highly crystalline COF simply by using the scCO₂ activation protocol. We therefore conclude that the TAPB-COF layers can be mobilized and shifted in all three dimensions upon exposure to external stimuli such as solvent vapors. This "breathing" feature of the frameworks results in a nearly complete amorphization in the case of fragile TAPB-COFs, while the robust TAPB-COFs resist a loss of order upon exposure to different solvents such as acetone, toluene and ethanol. Retrieving the structural order for these robust COFs can simply be achieved by the removal of the solvents by common means such as employing reduced pressure.

Among the solvents used in this study, 1,4-dioxane stands out by exhibiting a profound role in two different processes. This solvent is essential for the formation of the TAPBframeworks and is the main component in the solvent mixture for the synthesis of the bulk materials. However, it has a strong impact on the long-range order when used in postsynthetic solvent or vapor treatment for all of the fragile or robust structures examined. As none of the TAPB-COFs can withstand exposure to 1,4-dioxane, this is a general method for the deconstruction of highly crystalline and open porous TAPB-COFs. Even more remarkable, this process is reversible for every solvent or vapor used by employing a scCO₂ reactivation treatment whereby all TAPB-COFs regain their crystalline structure and their porosity (see Table S3 in Supporting Information).

To study the interactions of 1,4-dioxane with the COF frameworks, we conducted a theoretical study of the interactions of 1,4-dioxane with functional sites in the COF backbone. For the study, we chose molecular BDT-based dimers as model systems to mimic the BDT stacks in the COF backbone and imine motifs based on the TAPB scheme (Figures S59-

S62). Stable BDT dimers were surrounded by 1,4-dioxane to identify possible binding interactions. Two binding modes of 1,4-dioxane to the BDT-core, π -face or edge-on, were identified that give complexes that are competitive in energy (Figures S62, S63). Each BDT unit can accommodate two 1,4dioxane molecules or other oxygen containing molecules such as ethanol to give complex structures (Figure S62). Because edge-on coordination is the most relevant scenario for stacked oligomers in a COF, its effect on the stacking energy determines whether the solvent can dissociate the stacks. In the calculations, the 1,4-dioxane molecules in the BDT complex do not affect the stacking distance significantly but rather cause the BDT units to twist relative to each other (Figure S64). This weakens the stacking, so that the dimerization energy is calculated to be -25.8 and -19.6 kcal mol⁻¹ at MP2 and B3LYP-D3 level, respectively. These values compare with the dimerization energy with ethanol of -35.6 and -30.9 kcal mol⁻¹ at MP2 and B3LYP-D3 level, respectively. Thus, even in the absence of further solvent molecules, four 1,4 dioxane molecules weaken the stacking interaction significantly, particularly when compared to ethanol. Interestingly, we note that BDT-TAPB COF shows a certain stability towards EtOH exposure as depicted in Figure 2d. Our experiments also suggest that non-BDT TAPB COFs such as TA- and Py-2,7-TAPB COF also show lability towards 1,4-dioxane. Therefore, model calculations within Cs-symmetry on the coordination of chair dioxane to typical bonding moieties that occur in the COFs were carried out. These calculations gave the binding energies of 1,4-dioxane and are shown in Table S4. Moreover, to validate the hypothesis of specific binding of 1,4-dioxane onto the COF backbone, we examined, in a solvation experiment, the effect of a dioxane isomer, namely 1,3-dioxane, on a stable and crystalline BDT-OMe TAPB COF powder. Strikingly, the exposure of the COF powder to 1,3-dioxane had only a marginal effect on the crystallinity of the COF (Figure S21). This underlines that the specific interactions of 1,4dioxane with the backbone and this specific dioxane isomer is required for achieving the switch between the amorphous and crystalline COF phases (For detailed discussion see SI).

As the stacking of the TAPB-COFs can be modulated by employing solvent vapors and subsequent scCO₂ activation, we used 1,4-dioxane as an external stimulus for multiple activation and amorphization cycles. In a typical cycle, a highly crystalline and open porous scCO₂-activated COF powder was immersed in 1,4-dioxane for 24 h, filtered and dried under reduced pressure, resulting in the poorly crystalline, nonporous state (Figure S21a). Then, the poorly crystalline dried powder was scCO2-reactivated following the protocol described earlier. For all of the examined powders, the desired COF properties such as crystallinity and porosity were indeed restored in a comparable quality by the scCO₂ activation (Figure 4). This cycle was repeated several times, resulting in alternation between the crystalline, open porous and the poorly crystalline, non-porous COF states. Attempts at replacing the scCO₂ activation protocol with other activation methods, such as immersing the poorly crystalline robust COFs in a weaker solvent for the cycling experiments, failed to produce a powder with properties comparable to those resulting from the scCO₂ activation protocol (Figures S13, S14 and S21b).



Figure 4: a) Schematic model showing the effect of intercalation with solvent molecules on crystalline and ordered TAPB-COF layers. In the case of 1,4-dioxane acting as intercalated solvent molecules, the resulting framework does not retain order or porosity. Fragile COFs result in only short-range ordered and non-porous polymers, while robust COFs regain their order and porosity after removal of solvents. The PXRDs in (b) and (c) show the changes in crystallinity of the fragile BDT TAPB-COF over time after exposure to 1,4-dioxane (b) and EtOH (c) vapors. The PXRDs in (d) and (e) show the changes in crystallinity of the robust BDT-OMe TAPB-COF over time after exposure to 1,4-dioxane (d) and EtOH (e) vapors.

To exclude the possibility that only the pressure and the temperature of the scCO₂ activation is relevant for successful (re-)activation, a BDT TAPB-COF and a BDT-OMe TAPB-COF were treated with argon, simulating the CO₂ activation conditions concerning pressure and temperature. Notably, under these conditions argon is at a super critical state. These experiments yielded poorly crystalline materials indicating that scCO₂ has a crucial role in the dynamic process. Furthermore, we utilized scC_2H_6 as a hydrocarbon source for activation of BDT-OMe TAPB COF powder treated with 1,4dioxane. For the activation, the exact same activation conditions were applied as those for using scCO₂ or Ar. Notably, after the scC₂H₆ activation treatment the obtained powder did not feature crystallinity or substantial porosity. Modification of the CO₂ extraction protocol, employing temperature and pressure parameters that leave the CO₂ sub-critical, yielded poorly crystalline BDT-OMe TAPB COF powders. These experiments further support our conclusion that supercritical CO_2 plays a special role in enabling the recovery of the crystalline state (Figure S21).

Of particular interest is the recovery of TAPB-COFs from aqueous media, which would allow for efficient removal of polar guests captured within the porous structure. To study the behavior of the TAPB-COFs in an aqueous medium, we immersed a scCO₂-activated, fragile BDT TAPB-COF sample in deionized water (15 mg/5 mL, pH 7) for a period of 24 h. After the solvent treatment, the COF sample was filtered, dried under vacuum and examined by PXRD. As observed following the treatment with organic solvents, the PXRD of the water-treated fragile COF sample showed a complete loss of long-range order. This powder was then subjected to scCO₂ reactivation, resulting in the complete recovery of the COF structural order (Figure S20). As with organic solvents, the robust TAPB-COFs showed higher resistance to the water solvent treatment. After 24 h in water, the crystallinity of these robust COFs was still high as indicated by the observed reflections (Figures S6b and S8).

To gain further insights regarding the impact of the scCO₂ activation on the TAPB frameworks, we studied the interaction of poorly crystalline and crystalline COF powders with nitrogen and carbon dioxide by means of physisorption experiments. The porosity of the crystalline COF and of the corresponding poorly crystalline analog of the fragile BDT TAPB-COF were analyzed by N2 and CO2 adsorption measurements at 273 K and 1 bar. The crystalline BDT TAPB-COF displayed CO₂ uptake of 1.41 mmol/g and N₂ uptake of 0.57 mmol/g at 273 K (Figure 5). The powder was immersed in 1,4-dioxane (5 mg/mL) for 24 h yielding the short-range ordered BDT TAPB-COF analog after vacuum drying. This BDT TAPB-COF showed a lower N₂ uptake of 0.364 mmol/g. This can be attributed to the reduced surface area of the fragile COF due to fewer open pores. Interestingly, we observed that the short-range ordered COF analog displayed a significant increase in CO₂ uptake (1.94 mmol/g at 273 K), which is higher than that of the crystalline COF (Figure 5). This indicates a high affinity of CO₂ to the poorly crystalline framework and can possibly explain the effective activation of the COFs via $scCO_2$. We postulate that due to the smaller kinetic diameter of CO₂ (3.3 Å), as compared to N₂ (3.64 Å), CO₂ molecules are still able to access voids between displaced adjacent layers. In addition, these experiments illustrate the importance of controlling the framework characteristics, allowing for adjusting the interface affinity in the solid state.



Figure 5: Switching of N_2 (diamond) and CO_2 (circle) storage properties of BDT TAPB-COF upon 1,4-dioxane vapor treatment at 273 K. Red represents long-range ordered COF sample before vapor treatment, blue represents short-range ordered COF sample after the 1,4-dioxane vapor treatment.

CONCLUSION

In summary, we have shown that hexagonal imine COFs consisting of TAPB and different linear dialdehyde building blocks exhibit very different stabilities towards external stimuli. Freshly synthesized fragile TAPB-COFs instantly lose crystallinity and porosity upon exposure to solvents, heat or vacuum. We attribute the sensitivity of these COFs mainly to weaker π - π interactions of the linear dialdehydes between adjacent layers. We found that the fragile TAPB-COFs can be stabilized by the incorporation of alkoxy substituents on the BDT-cores. While the usual extraction workup strategies for the fragile TAPB-COFs failed, we developed a successful workup procedure based on scCO₂ extraction for these fragile as well as the robust TAPB-COFs of our test series. The scCO₂ extraction is not only a fast and efficient process, but it also minimizes the amount of solvents needed in the workup procedure.

Furthermore, we have established that successfully scCO₂activated, highly crystalline and open porous COFs can be completely converted into poorly crystalline and non-porous polymers by exposure to solvents in liquid and vapor phases. Intriguingly, this process is completely reversible by applying the scCO₂ activation approach, and the crystalline/short-range ordered switching cycle can be repeated many times. The dramatic transformation of fragile COFs from the crystalline to the poorly crystalline state also leads to substantial changes in the gas adsorption behavior. Hence, the 1,4-dioxane treated, poorly crystalline BDT TAPB-COF shows a higher CO2 to N2 uptake ratio for adsorption in comparison to the crystalline analog at 1 bar pressure (~6.3 vs ~2.9, Figure 5). Therefore, as CO₂ is still able to access the voids in-between displaced COF layers, in its supercritical state it allows for a full reconstruction of the poorly crystalline, non-porous polymer into a crystalline and open-porous COF. In view of the above, our results provide deeper insight into the decisive role of subtle interlayer interactions in determining the porosity and crystallinity of COFs.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXXXX

The Supporting Information contains detailed information on synthetic procedures, work-up approaches, and structural investigations of the TAPB-COFs.

AUTHOR INFORMATION

Corresponding Author

<u>*dana.medina@cup.uni-muenchen.de</u> *bein@lmu.de

Notes

The authors declare no competing financial interest.

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Supercritical CO₂

ON ↔ OFF Interlayer Correlation Porosity

Drying





57x44mm (300 x 300 DPI)