

Mild and Scalable Conditions for the Solvothermal Synthesis of Imine-Linked Covalent Organic Frameworks

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A convenient method was developed that allows for the synthesis of highly crystalline and porous imine-linked covalent organic frameworks (COFs) in hours. The use of an apolar solvent in combination with a precise amount of water and acetic acid was crucial to obtain materials of optimal quality. Fifteen different COFs could be produced under the same reaction conditions, using a green solvent mixture of n-butanol, acetic acid and water at 70 °C for 16 hours with stirring. The crystallinity of the COFs produced in this manner is similar or better than that obtained by traditional solvothermal synthesis. The method could be easily scaled to synthesize over ten grams of COF in one batch. Optical microscopy, FTIR spectroscopy and *in situ* Raman spectroscopy gave insight in the role of the solvent on the aggregation of COF nanosheets and the resulting crystallinity, porosity and robustness of the material.

Introduction

Covalent organic frameworks (COFs) are crystalline porous networks consisting of organic monomers that are linked together via a reversible reaction. The chemical properties of the framework depend both on the monomers and type of linkage. Due to their intrinsic nanoporosity, exceptional surface area, well-defined structure and tunability, COFs have been reported for applications in a wide range of fields, including adsorption, separation, catalysis, sensing, energy storage, and luminescence^[1–4]. Despite the intense research interest, there are as of yet no large companies commercially producing COFs for industrial applications. The closely related metal-organic frameworks (MOFs) did make an industrial breakthrough: BASF is producing several hundred tons of CALF-20 per year as of 2023, to be used for carbon capture^[5,6]. We believe this difference in industrial advance is for a large part rooted in the lack of a convenient and scalable synthesis method for COFs.

Recently, there have been attempts to overcome this issue. Notable to mention here is YOCOF Material, a small company founded in 2023 specializing in the synthesis of COFs on large scale for industrial applications^[7]. The company relies for this on the melt synthesis procedure developed by Zhenjie et al. This method uses a flux of molten benzoic anhydride at 180 °C to produce crystalline vinylene-linked COFs, or molten benzoic acid at 200–250 °C to produce imide-linked COFs on gram-scale^[8,9]. The same groups also reported the synthesis of imine-linked COFs in a melt of benzoic anhydride at 120 °C. Under these conditions, they demonstrated the synthesis of five

different COFs, however the crystallinity and porosity of these COFs was inferior to those obtained by solvothermal synthesis^[10]. Also important in this context is the work of Banerjee et al., who have made several reports on the solvent-free synthesis of β -ketoenamine COFs, using p-toluenesulfonic acid as catalyst. Their process could be successfully scaled to the multi-gram scale, and the resultant materials exhibit high porosity^[11,12]. However, this study focused solely on β -ketoenamine COFs, starting from 1,3,5-triformylphloroglucinol as the aldehyde monomer. Finally, there have been some efforts in recent years to produce single-crystalline COFs. Zhou et al. discovered that several single-crystalline 3D COFs could be grown in water on gram-scale under ambient conditions, using amphiphilic amino-acid derivatives to form micelles which aid the crystallization^[13]. The reaction required 3 to 14 days to produce single crystals. The authors also tested their method for one two-dimensional COF, which was obtained as a polycrystalline powder with good crystallinity and porosity.

Nonetheless, the majority of imine-linked COFs, by far the most studied type, are still synthesized on a milligram scale using solvothermal protocols. A typical COF synthesis is performed at 120 °C for 72 hours or longer. To prevent possible oxidation of monomers under these harsh conditions, the solvent is thoroughly degassed by freeze-pump-thawing, usually in glass ampoules which are then flame-sealed before heating^[14]. Each combination of monomers typically requires a distinct solvent combination to yield a COF of optimal quality. This time-consuming process hampers the quick development of new COFs. Common solvents are combinations of 1,4-dioxane, mesitylene, n-butanol, o-dichlorobenzene and *N,N*-dimethylacetamide. With the exception of n-butanol, these solvents are all relatively expensive and pose a health hazard. These factors make scalability an issue: reports on gram-scale synthesis of imine-linked COFs are quite scarce^[15–19].

Sporadic research has focused on developing milder conditions for COF synthesis. Many of these studies present new catalysts for COF formation, such as transition metal triflates, nitrates or oxides, organic Lewis acids or hydroxide bases^[20–24]. While these catalysts can indeed produce certain crystalline COFs, their applicability was only demonstrated for a limited range of monomers: many of the COFs produced with these catalysts were shown to have lower crystallinity and porosity than those made with classical solvothermal synthesis. On top of that, these alternative catalysts are often significantly more expensive than acetic acid. Other reported strategies are (1) the use of monofunctional organic modulators, such as aniline or benzaldehyde, to enhance error correction, (2) the introduction of certain additives, such as Triton X-100 or imidazole, in the reac-

tion mixture (3) prefunctionalization of the monomer, for example by conversion of the monomer amine groups to N-aryl benzophenone imines^[18,19,25–28]. Besides the problems mentioned above, the methods also give rise to an extra synthetic cost and additional waste.

A relatively recent breakthrough is sonochemical synthesis, discovered by Zhao et al.^[29]. Using ultrasonication, a range of COFs can be produced at room temperature in aqueous acetic acid. This elegant method requires no heating nor any organic solvents other than ecofriendly acetic acid. However, the sonication power and acetic acid concentration still had to be optimized for each COF. Although the method could produce many COFs in some cases, the yield, crystallinity, or porosity were inferior to that of their solvothermal counterparts. Furthermore, the method uses an ultrasonication microtip probe, equipment that is rarely available in a common lab and has yet to be employed in industrial chemistry. The authors scaled up the synthesis of one COF to 500 mg. The scaled COF had the same crystallinity and porosity as the small-scale reaction, but the yield dropped by over 20%.

Results and Discussion

In this study, we set out to find a set of conditions under which COFs will form with high crystallinity and porosity. We chose to use green and inexpensive aqueous alcohol solutions as the solvent, and acetic acid as the catalyst, under aerobic conditions. The combination of 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 2,5-dibromoterephthalaldehyde (TaBr₂) yields the COF TAPB–TaBr₂. This COF has been reported to be resilient to pore collapse, which removes the need for mild activation^[30]. The COF was synthesized in a simple cap-closed vial under ambient atmosphere. We stirred the reaction to mitigate the effect of differing solubility of the monomers in different solvent mixtures. Five parameters were optimized: the carbon number of the alkyl alcohol (1–10), the reaction time, reaction temperature, and water and acid content of the mixture. The obtained materials were characterized by PXRD and N₂-sorption, and are shown in **Figure 1** for n-butanol as the best-performing alcohol and **Figure 2** for the alcohol alkyl chain length effect. Synthetic details of the different optimization attempts are given in **Table S1**.

Systematic variation of the water content between 0 v% and 60 v% showed an optimum at 10 v% water (**Figure 1A, D**). Water allows for the hydrolysis of formed imine bond and thus improves error correction during COF formation. A too high water content however can drive the imine formation equilibrium towards the reactants, which hampers the formation of an ordered framework. The acid content of the reaction mixture played a major role in the COF crystallization process (**Figure 1B, E**). With an acid content of 1 M (based on the total solvent volume), a poorly crystalline and porous material was obtained. The COF quality increases with increasing acetic acid content, up to 4 M. This agrees with the well-known fact that acetic acid catalyzes the reversible imine bond formation. However, beyond 4 M the COF quality started to decrease again. A clear trend was seen for the influence of the reaction temperature: synthesis at 70 °C yielded materials of markedly higher quality than those made at 20 °C. Further increase of the temperature to 120 °C only marginally enhanced the COF quality (**Figure 1C, G**). A COF of excellent quality was already

formed after 16 hours of reaction. Increasing the reaction time led only to a minor improvement of crystalline features: the PXRD patterns of TAPB–TaBr₂ synthesized in 16 hours and 72 hours were very similar. However, with only 4 hours reaction time, the material showed significantly lower crystallinity (**Figure 1D, H**).

The porosity and crystallinity of TAPB–TaBr₂ increased with increasing carbon number of the alcohol up to four, from a nearly amorphous and nonporous material in methanol, to a high-quality COF in n-butanol with a BET surface area exceeding 1300 m²/g (**Figure 2C**). Literature synthesis of this COF yielded a material with very similar surface area, but took 3 days at 120 °C in degassed o-dichlorobenzene^[31,32]. Synthesis of TAPB–TaBr₂ in n-hexanol and n-octanol-containing mixtures gave similar results as n-butanol. The mixture of n-decanol, water, and acetic acid was no longer homogeneous, even at 70 °C. We believe this phase separation explains the decrease in COF quality.

To rationalize the difference in COF quality between methanol and n-butanol as solvents, we investigated the COF formation *in situ* using Raman spectroscopy over the course of 12 hours (**Figure 3A, B**) in mixture of methanol, respectively n-butanol with 10 v% water and 4 M acetic acid. In both cases, the aldehyde C=O stretching vibration of TaBr₂ around 1690 cm^{−1} and the C–H stretching vibration of TAPB around 1360 cm^{−1} disappeared within less than 2 minutes. A new intense peak occurred at 1570 cm^{−1}, which we ascribe to the phenyl C=C stretching vibration of the COF network. This peak is accompanied by a smaller C=N stretching vibration at 1616 cm^{−1}, indicative of imine bond formation^[33]. Within less than 10 minutes, the measured spectrum was nearly identical to that of the finished and dried COF. In line with this observation, the reaction yield, calculated based on the weight of the COF, reached more than 90% after 10 minutes and hardly increased further (**Figure S67**). This indicates that polymerization was nearly finished within a few minutes regardless of the solvent. However, over the next hours the overall Raman spectrum increased in intensity in both solvents. A plot of the intensity of the peak at 1570 cm^{−1} is given in **Figure 3C**. The gradual increase in overall Raman intensity is much more outspoken for the reaction in n-butanol than that in methanol.

We found that the cause for this increased intensity finds its origin in a difference in particle growth over time in the two solvents. It has been reported that larger particles give rise to higher Raman intensity^[34]. When we correct for the influence of particle size using standard normal variate (SNV) correction, we found that the Raman intensity for the peak at 1570 cm^{−1} increased up until around 10 minutes, and then remained constant, in line with the yields of the COF reaction (**Figure S66, Figure S67**). To support this hypothesis, we visually observed the aggregation of COF particles with optical microscopy (**Figure 3E**). During the synthesis process, small aliquots of COF were taken from the vials, and gently pressed between two glass slides while still soaked with solvent. The images show clearly that in n-butanol, the COF particles aggregate over time to form larger particles. The average size of the COF aggregates is much smaller in methanol at any given point in time. SEM images of the COF particles after reaction, washing and drying confirm the same trend (**Figure S70, Figure**

S71). The difference in morphology could even be observed with the naked eye at the end of the reaction. The reaction in methanol yielded a dense, sand-like powder resting at the bottom of the vial, while in n-butanol we saw a voluminous fluffy powder which somewhat floated in the solvent.

We furthermore investigated the changes in the FTIR-spectra of the COFs over time. Small aliquots were taken from the reaction at four points in time and thoroughly filtered, washed and dried before measurement, to assure all unreacted monomers were removed. Notably, the peaks at 3355 and 3205 cm^{-1} , 1517 cm^{-1} and 1282 cm^{-1} decrease in intensity as the reaction time progresses (**Figure 3D**, **Figure S18**). We hypothesize these peaks originate respectively from the N-H stretching vibrations, C-H rocking vibration and the C-N stretching vibrations of terminal TAPB-moieties located at the edge of a COF nanosheet, where one or two of the amine groups are still present. With n-butanol as a reaction solvent, these peaks diminish quickly over time and have almost completely disappeared after 12 hours. In methanol the peak intensity decreases much slower, and all four peaks are still well visible even after 12 hours of reaction.

From these combined observations, we propose a possible explanation for the divergent COF formation in the two solvents, building on the mechanism proposed by Feriante et al. (**Figure 4A**)^[35]. Due to the magnetic stirring, the monomers are quickly distributed evenly over the solvent. The presence of a large amount of catalytic acid allows for fast, near complete formation of COF nanosheets via imine condensation. The newly formed nanosheets are protonated at the edges, as a result of the dynamic imine condensation equilibrium with the surrounding acidic environment. These positive charges repel one another and in this way disrupt the ordered stacking of the COF nanosheets^[35]. This is consistent with the observation that at higher acetic acid concentrations the crystallinity of the resultant COF decreased (**Figure 1B**). Due to the apolar butyl group, these edge-protonated nanosheets will tend to clump together in n-butanol. The close proximity of nanosheets stimulates them to stitch together. By this we mean that terminal aldehyde and amine groups on the edges of the nanosheets react with each other to form a larger nanosheet. The now larger nanosheets have a lower ratio of protonated edges to total surface area, which reduces the overall repulsion between the sheets and thus increases their tendency to stack in an ordered fashion. In the more polar methanol-containing mixture, the protonated nanosheets are more effectively dispersed and therefore less prone to aggregation. This results in the COF nanosheets stitching together slower over time. The smaller particles have a higher edge to surface ratio, and thus more protonated sites per nanosheets surface, counteracting the ordered stacking of the nanosheets. Such smaller particles as a result should have more exposed edges which contain unreacted terminal aldehyde and amine groups, as we indeed observed from FTIR-spectroscopy (**Figure 3D**). We could further confirm this mechanism with observations from transmission electron microscopy (TEM) measurements. In both methanol and n-butanol, COF nanosheets can be seen. However, the nanosheets in n-butanol are much larger than the sheets in methanol (**Figure S72**, **S73**).

The difference in particle size and consequently ordered stacking has a pronounced effect on the robustness of the COF. Feriante et al. discovered that properly stacked COFs are more resilient to pore collapse^[36]. We could confirm these findings by stopping the synthesis in n-butanol at 70 °C after one hour, and mildly activating the COF with a low surface tension solvent to prevent possible pore collapse (**Figure 4B**). The resulting material was highly crystalline even after 1 hour, while we previously found that the same COF synthesized in 4 hours with vacuum activation was only weakly crystalline (**Figure 1D**). In methanol, TAPB-TaBr₂ synthesized in one hour yielded a material of poor quality even with mild activation. After 16 hours, a similarly poorly crystalline material was obtained after vacuum activation, but mild activation gave a COF of high crystallinity (**Figure 4B**). Previous reports have already described how the robustness of a COF depends on pore size, architecture and functionality and synthesis time^[30,36]. We can now add that the right solvent is also crucial to promote robustness: faster stitching in n-butanol compared to methanol leads to far more robust Ta-TaBr₂ particles.

We have now established that alcohols with a long apolar linear alkyl chain, but still miscible with aqueous acetic acid are optimal to promote the growth of TAPB-TaBr₂. Control experiments were done to see if the same effect can be achieved using other solvents. We tried benzyl alcohol and benzonitrile with 10 v% water and 4 M acetic acid, and obtained highly crystalline TAPB-TaBr₂ in both cases (**Figure 4C**). Alcohols and nitriles allow here for miscibility via hydrogen bonding, while the apolar benzylgroup promotes COF stitching. Both the apolar group and the miscibility are necessary: synthesis in mixtures with the very polar N-methylpyrrolidone (NMP) yielded a nearly amorphous polymer. The other extreme, a stirred emulsion with apolar n-hexane gave a COF of poor crystallinity as well (**Figure 4C**).

Synthesis in the linear alkyl alcohols from n-propanol to n-octanol gave very similar results for TAPB-TaBr₂. From these options, we chose to continue with n-butanol because it is both a green solvent and a cheap commodity chemical, which can be produced from biomass^[37], and because it yielded a COF with a slightly higher BET surface area. Using the optimal set of reaction conditions, we attempted to synthesize an additional 15 COFs. We performed the reactions at 70 °C in n-butanol with 10 v% H₂O and 4 M AcOH. The reactions were done for 16 hours, to give the COF particles more time to grow and become less prone to pore collapse. For every COF, the Pawley refined PXRD pattern corresponded well to the theoretical structure (**Section S6**). Successful formation was also confirmed by FTIR, which showed the presence of the imine stretching vibration around 1600-1620 cm^{-1} , and by N₂-sorption (**Section S4**, **Section S5**). A comparison of the BET surface area's and yields of the COFs obtained by our method and some of the best literature results can be found in **Table S4**, **Figure S49**, **S50**. Both variations in the aldehyde and amine linkers gave COFs with excellent crystallinity. The method proved to be successful for the synthesis of COFs of different topology, such as [3+3] and [4+2] combinations (**Figure 5E**, **G**, **H**, **I**, **J**, **K**, **N**, **O**). When using electron-rich 1,4-phenylenediamine (PDA),

we found it necessary to perform the reaction under an inert atmosphere with degassed solvent to avoid aerobic oxidation of the linker (**Figure 5I, M**). Interestingly, although stacking does not occur in 3D COFs, COF-300 could also be synthesized under these conditions with good crystallinity, but was obtained in the hydrated state, which has a very low surface area^[38,39]. (**Figure 5J**). In the case of TAPT-IP, a geometrically challenging COF with a dialdehyde monomer where both aldehydes are not oriented along the same axis, the BET surface area of 570 m²/g exceeded that of the same COF made by both solvothermal and sonochemical methods (**Figure 5L**)^[29,40]. We further synthesized a COF with the sterically hindered aldehyde monomer 2,4,6-trimethylbenzene-1,3,5-tricarbaldehyde (TFM) (**Figure 5M**) and the highly nitrogen-rich heterocyclic monomer 4,4',4''-(tris([1,2,4]triazolo)-[1,3,5]-triazine-tribenzaldehyde (TTT) (**Figure 5N**). We also produced a new COF, based on TAPPy and 2,5-dimethylpyrazine-3,6-dicarboxaldehyde (Pyz) with outstanding crystallinity and porosity (**Figure 5O**). The use of 1,3,5-triformylphloroglucinol (Tp) as the aldehyde linker yielded a COF of weak crystallinity (**Figure 5P**). We believe the conditions described here are not suited to ensure sufficient error correction due to the poor reversibility of the stable β -keto-enamine bonds. The structurally similar TAPT-TFPO COF, which contains only one hydroxyl group on the aldehyde monomer, did show strong crystalline features in its PXRD pattern (**Figure 5K**).

Our synthesis method could also be used for the synthesis of known fragile COFs. We opted for diethyl ether as a low-surface tension solvent for mild activation instead of the previously reported supercritical CO₂, hexane or perfluorohexane. Diethyl ether has a lower surface tension ($\gamma = 17.15$ mN/m at 25 °C) than n-hexane ($\gamma = 18.43$ mN/m), but is less environmentally damaging than n-hexane or perfluorohexane, and can, contrary to supercritical CO₂, be used at ambient pressure. The BET surface area of TAPB-Ta (2107 m²/g) made in this manner was comparable to that of COFs activated with supercritical CO₂ (2097 m²/g), hexane (2060 m²/g) or perfluorohexane (2121 m²/g)^[41].

Because of the cheap solvent and catalyst and the convenient synthetic conditions, our method allows for facile synthesis of COFs on a multigram scale. We could synthesize more than 10 grams of TAPT-TaMe₂ COF in one batch by simply scaling the monomer and solvent amount. The COF was obtained in 88% yield and showed a nearly identical crystallinity as the small-scale synthesis, indicating the potential of this method for the synthesis of COFs on an industrial scale. We also scaled up the synthesis of TAPB-TaBr₂ and PDA-TFPPy to over one gram, with retention of the crystallinity of the small-scale reaction (**Section S8**).

Conclusion

This work demonstrated that a wide variety of imine-linked covalent organic frameworks can be made in simple aqueous solutions of alkyl alcohols with acetic acid under mild conditions. Synthesis in alcohols with a carbon number higher than four produced well-ordered COFs, while in ethanol and methanol poorly crystalline polymers were obtained. A combination of Raman spectroscopy, optical microscopy, PXRD and FTIR analysis indicated that alcohols

with long alkyl chains promote efficient stitching of the COF nanosheets, leading to larger and well-stacked COF particles which resist pore collapse. We find this effect can be obtained by using in general a solvent with an apolar group that is still miscible with aqueous acetic acid. The green solvent combination of n-butanol, water and acetic acid was used to generate a variety of COFs under the same conditions with high crystallinity. This work proves that a broad range of highly crystalline COFs can be made without the use of ampoules, high temperatures, expensive solvents, additives, or specialized catalysts. Rigorous exclusion of oxygen was also shown to be redundant in many COF syntheses. The method could moreover be easily scaled to the decagram scale. The possibility to produce COFs on a large scale allows future researchers to test them for practical applications on an industrial level. For example, TAPB-Ta, one of the best performing COFs for photocatalytic H₂O₂ generation^[42], could be scaled and tested as a prototype for industrial H₂O₂ production. Other possible future avenues of research might be the scale-up of imine COFs synthesis to the kilogram scale and beyond, or an in-depth technoeconomic analysis of the cost of production of imine COFs, similar to what has been reported for MOFs^[43]. We sincerely hope this discovery will simplify the development of new useful covalent organic frameworks and expedite their transition to industrial relevance.

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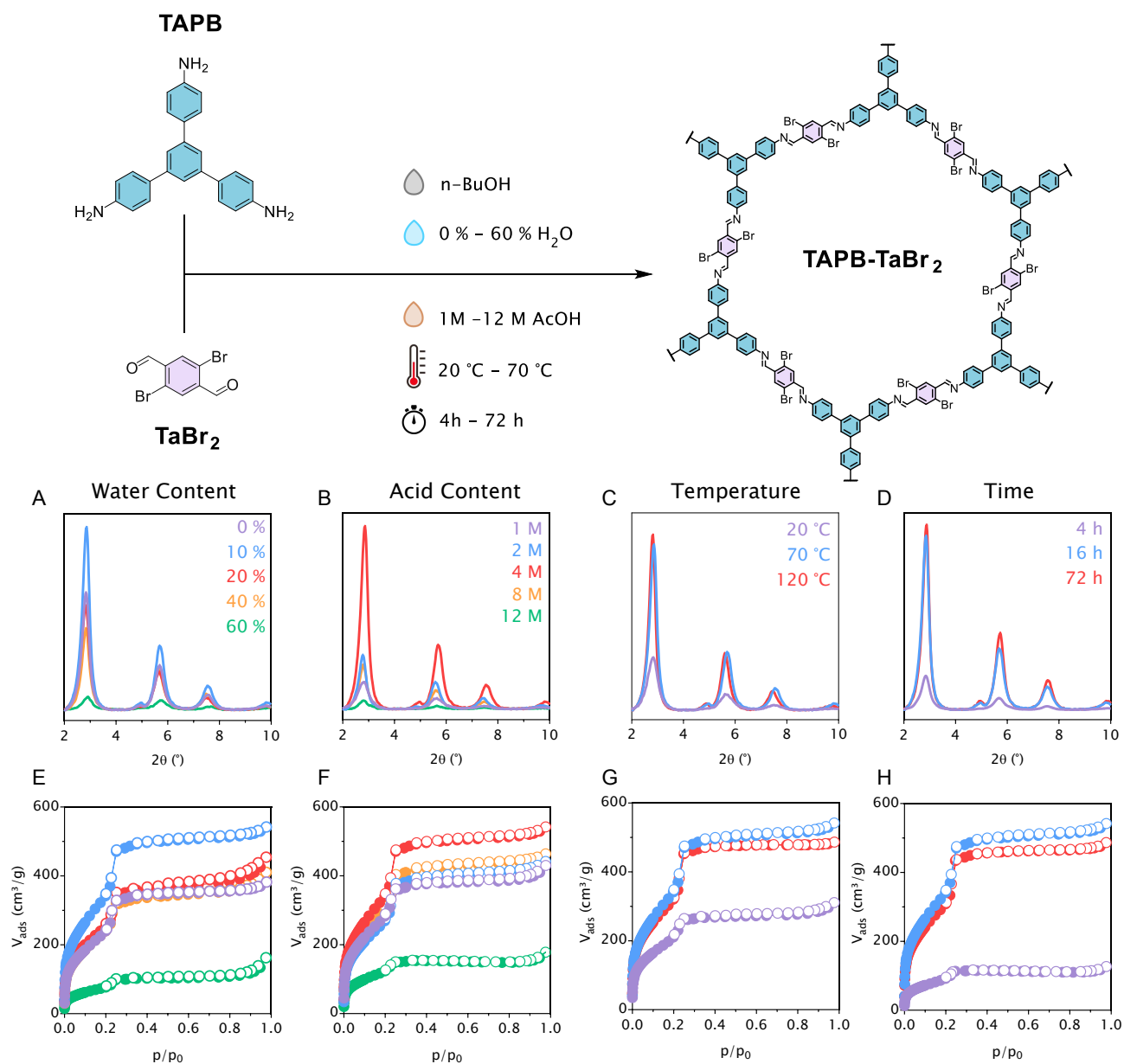


Figure 1. PXRD patterns and N₂-sorption isotherms of TAPB-TaBr₂ COF synthesized in n-BuOH with variation of the water content (A,E), acetic acid content (B,F), reaction temperature (C,G) and time (D,H) from base parameters (10 v% H₂O, 4 M AcOH, 16 h, 70 °C).

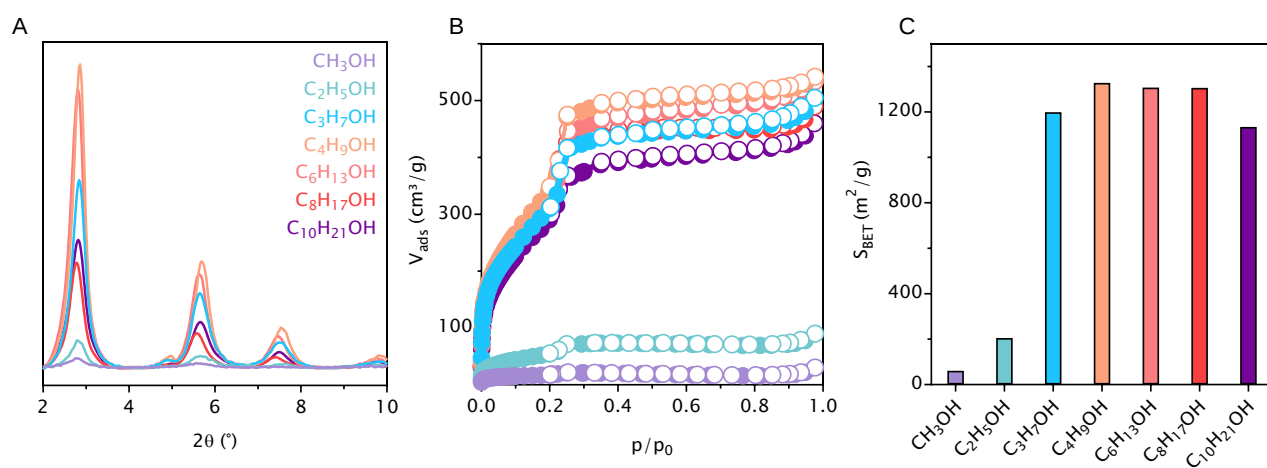


Figure 2. The PXRD patterns, N₂-sorption isotherms, and calculated S_{BET} of TAPB-TaBr₂ synthesized using different alkyl alcohols

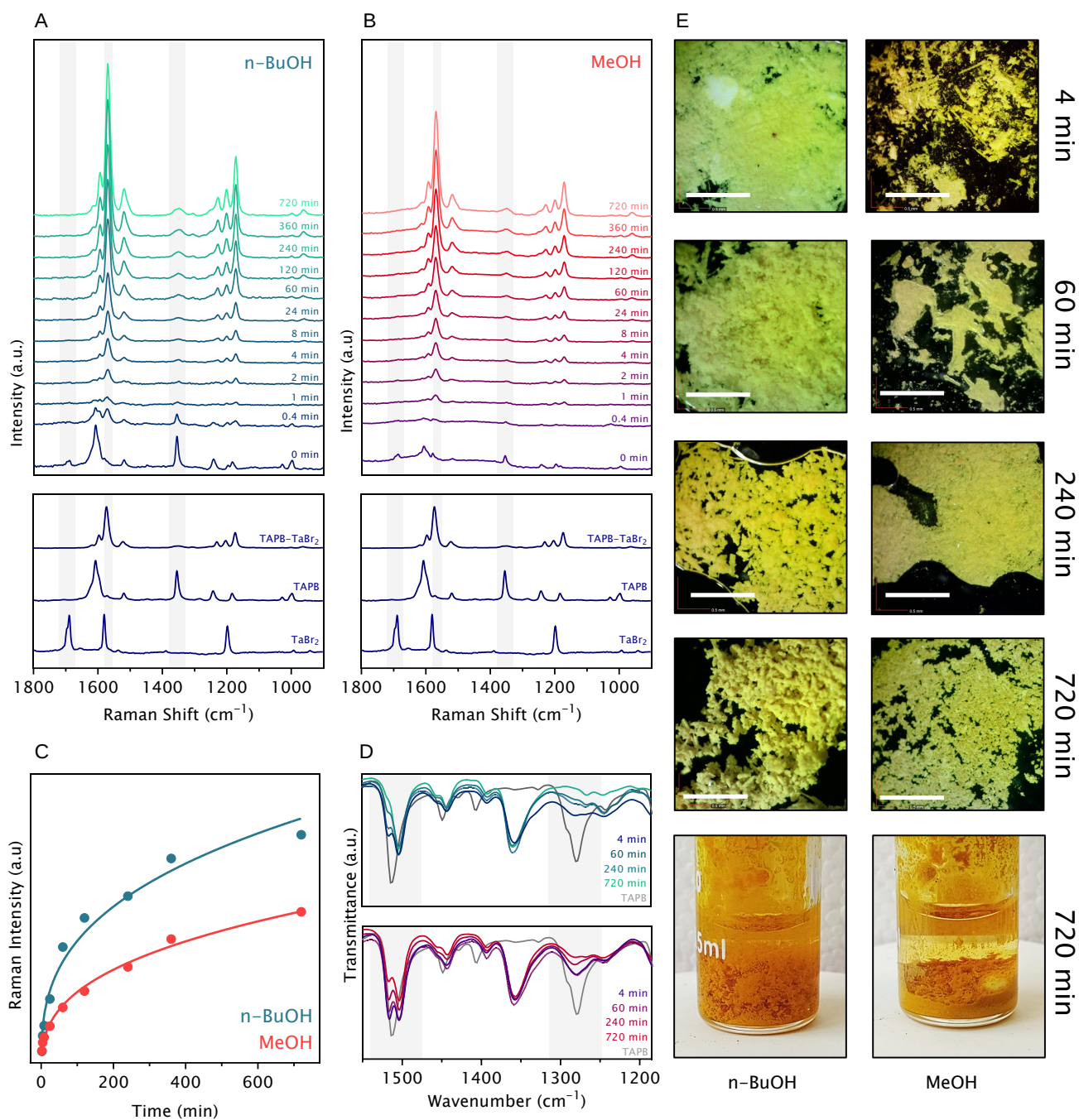


Figure 3. Evolution over time of the Raman spectrum of a mixture of TAPB and TaBr₂ in (A) n-butanol and (B) methanol; The intensity of the C=C stretch at 1570 cm⁻¹ over time of the reaction mixture containing n-BuOH (teal) or methanol (red) (C); FTIR spectra of the washed and dried TAPB-TaBr₂ synthesised in reaction mixtures with n-butanol (top) or methanol (bottom) (D); Optical microscopy images and photographs of TAPB-TaBr₂ during synthesis in n-butanol (left) or methanol (right) at different points in time. The white bar is 1 mm. (E)

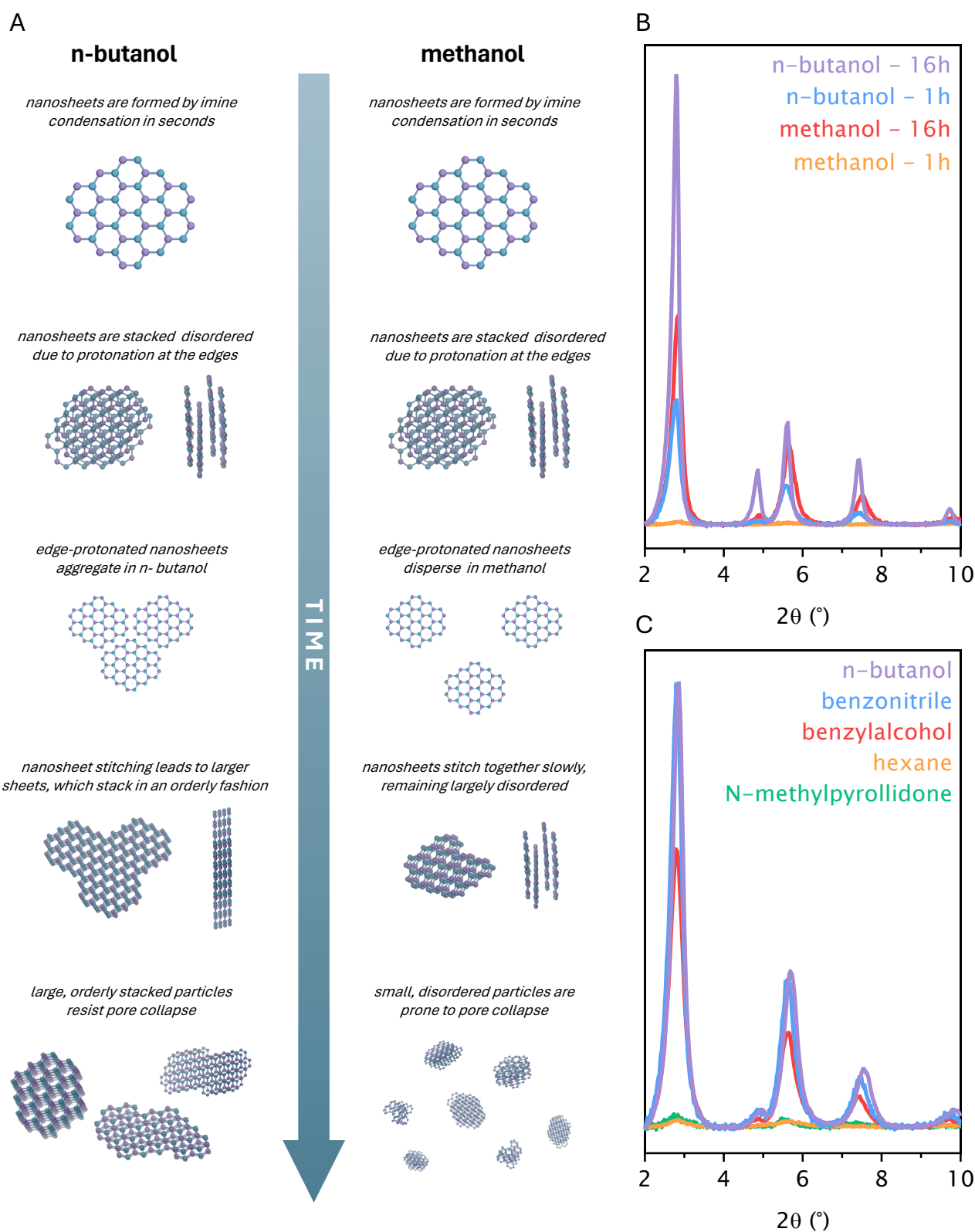


Figure 4. Proposed mechanism for the synthesis of COFs in a mixture containing n-butanol (left), or methanol (right) (A); Synthesis of TAPB-TaBr₂ with mild activation, showing the influence of reaction time and solvent on the robustness of the COF (B); TAPB-TaBr₂ synthesized in mixtures of n-butanol, benzonitrile, benzylalcohol, hexane or N-methylpyrrolidone with 10 v% water and 4 M acetic acid (C).

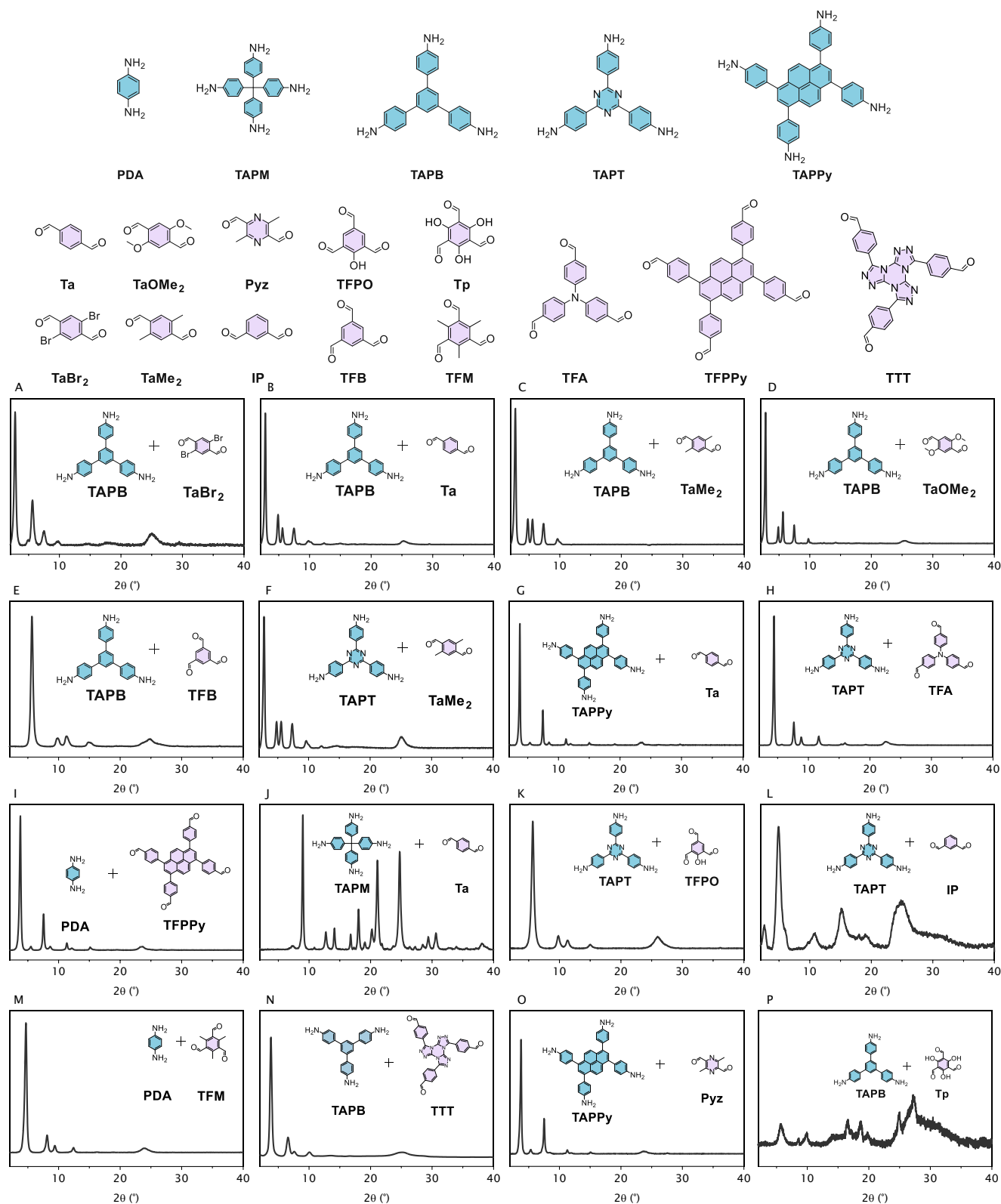


Figure 5. Overview of the different monomers and PXRD patterns of the 16 attempted COFs

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Conflict of Interest

The authors declare no conflict of interest.

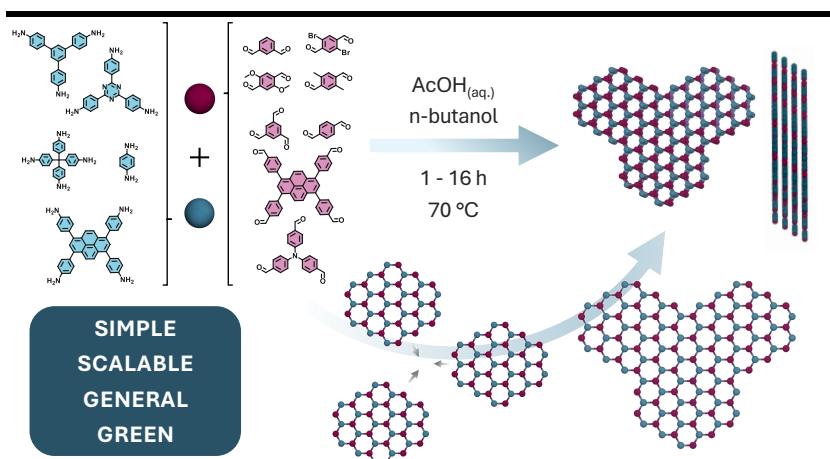
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References

- [1] Z. Wang, S. Zhang, Y. Chen, Z. Zhang, S. Ma, *Chemical Society Reviews* **2020**, *49*, 708.
- [2] X. Zhao, P. Pachfule, A. Thomas, *Chemical Society Reviews* **2021**, *50*, 6871.
- [3] D.-G. Wang, T. Qiu, W. Guo, Z. Liang, H. Tabassum, D. Xia, R. Zou, *Energy & Environmental Science* **2021**, *14*, 688.
- [4] W. K. Haug, E. M. Moscarello, E. R. Wolfson, P. L. McGrier, *Chemical Society Reviews* **2020**, *49*, 839.
- [5] K. Hoffmann, BASF becomes first company to successfully produce metal organic frameworks on a commercial scale for carbon capture **2023**, https://www.basf.com/global/documents/en/news-and-media/news-releases/2023/10/P327e_MOFs_Svante.pdf [Accessed: (14/05/2024)].
- [6] C. Nitta, Svante Secures Commercial Supply of MOF **2023**, <https://www.svanteinc.com/press-releases/svante-secures-commercial-supply-of-mof-advanced-sorbent-materials-with-basf-for-carbon-capture-market/> [Accessed: (25/05/2024)].
- [7] Y. M. S. C. LTD., YOCOF MATERIAL (SUZHOU) CO. LTD. **2023**, <https://en.yocofs.com> [Accessed: (18/08/2024)].
- [8] Z. Wang, Y. Zhang, T. Wang, L. Hao, E. Lin, Y. Chen, P. Cheng, Z. Zhang, *Chem* **2023**, *9*, 2178.
- [9] P. Zhang, Z. Wang, Y. Yang, S. Wang, T. Wang, J. Liu, P. Cheng, Y. Chen, Z. Zhang, *Science China Chemistry* **2022**, *65*, 1173.
- [10] Y. Zhang, T. Mao, L. Hao, T. Sun, T. Wang, P. Cheng, Y. Chen, Z. Wang, Z. Zhang, *Macromolecular Rapid Communications* **2023**, *44*, 2200722.
- [11] S. Karak, S. Kandambeth, B. P. Biswal, H. S. Sasmal, S. Kumar, P. Pachfule, R. Banerjee, *Journal of the American Chemical Society* **2017**, *139*, 1856.
- [12] B. P. Biswal, S. Chandra, S. Kandambeth, B. Lukose, T. Heine, R. Banerjee, *Journal of the American Chemical Society* **2013**, *135*, 5328.
- [13] Z. Zhou, L. Zhang, Y. Yang, I. J. Vitorica-Yrezabal, H. Wang, F. Tan, L. Gong, Y. Li, P. Chen, X. Dong, et al., *Nature Chemistry* **2023**, *15*, 841.
- [14] K. Geng, T. He, R. Liu, S. Dalapati, K. T. Tan, Z. Li, S. Tao, Y. Gong, Q. Jiang, D. Jiang, *Chemical reviews* **2020**, *120*, 8814.
- [15] L. Xu, S.-Y. Ding, J. Liu, J. Sun, W. Wang, Q.-Y. Zheng, *Chemical communications* **2016**, *52*, 4706.
- [16] X.-H. Han, J.-Q. Chu, W.-Z. Wang, Q.-Y. Qi, X. Zhao, *Chinese Chemical Letters* **2022**, *33*, 2464.
- [17] Y. Zhang, T. Mao, L. Hao, T. Sun, T. Wang, P. Cheng, Y. Chen, Z. Wang, Z. Zhang, *Macromolecular Rapid Communications* **2023**, *44*, 2200722.
- [18] L. Guo, Q. Y. Zhang, Z. Yu, R. Krishna, F. Luo, *Chemistry of Materials* **2023**, *35*, 5648.
- [19] F. Tan, Y. Zheng, Z. Zhou, H. Wang, X. Dong, J. Yang, Z. Ou, H. Qi, W. Liu, Z. Zheng, et al., *CCS Chemistry* **2022**, *4*, 3751.
- [20] M. Matsumoto, R. R. Dasari, W. Ji, C. H. Feriante, T. C. Parker, S. R. Marder, W. R. Dichtel, *Journal of the American Chemical Society* **2017**, *139*, 4999.
- [21] D. Zhu, Z. Zhang, L. B. Alemany, Y. Li, N. Nnorom, M. Barnes, S. Khalil, M. M. Rahman, P. M. Ajayan, R. Verduzco, *Chemistry of Materials* **2021**, *33*, 3394.
- [22] Y. Zhu, D. Zhu, Q. Yan, G. Gao, J. Xu, Y. Liu, S. B. Alahakoon, M. M. Rahman, P. M. Ajayan, E. Egar, et al., *Chemistry of Materials* **2021**, *33*, 6158.
- [23] X. Shi, L. Yi, H. Deng, *Science China Chemistry* **2022**, *65*, 1315.
- [24] L. Zhang, R. Liang, C. Hang, H. Wang, L. Sun, L. Xu, D. Liu, Z. Zhang, X. Zhang, F. Chang, et al., *Green chemistry* **2020**, *22*, 2498.
- [25] D. Zhu, L. B. Alemany, W. Guo, R. Verduzco, *Polymer Chemistry* **2020**, *11*, 4464.
- [26] E. Dautzenberg, F. W. Claassen, L. C. de Smet, *Microporous and Mesoporous Materials* **2023**, *350*, 112318.
- [27] E. Vitaku, W. R. Dichtel, *Journal of the American Chemical Society* **2017**, *139*, 12911.
- [28] J. Sprachmann, N. Grabicki, A. Möckel, J. Maltitz, J. R. Monroy, G. J. Smales, O. Dumele, *Chemical Communications* **2023**, *59*, 13639.
- [29] W. Zhao, P. Yan, H. Yang, M. Bahri, A. M. James, H. Chen, L. Liu, B. Li, Z. Pang, R. Clowes, *Nature Synthesis* **2022**, *1*, 87.
- [30] D. Zhu, J.-J. Zhang, X. Wu, Q. Yan, F. Liu, Y. Zhu, X. Gao, M. M. Rahman, B. I. Yakobson, P. M. Ajayan, et al., *Chemical Science* **2022**, *13*, 9655.
- [31] Q. Liu, Q. Liao, J. Hu, K. Xi, Y. Wu, X. Hu, *Journal of Materials Chemistry A* **2022**, *10*, 7333.
- [32] L. Zhao, X. Tang, X. Ni, J. Zhang, G. Ineza Urugeni, D. Wang, H. He, P. Dramou, *Langmuir* **2024**, *40*, 1884.
- [33] S. K. Schoustra, M. H. de Heer Kloots, J. Posthuma, D. Van Doorn, J. A. Dijkstra, M. M. Smulders, *Macromolecules* **2022**, *55*, 10341.
- [34] M. Gen, C. K. Chan, *Atmospheric Chemistry and Physics* **2017**, *17*, 14025.
- [35] C. Feriante, A. M. Evans, S. Jhulki, I. Castano, M. J. Strauss, S. Barlow, W. R. Dichtel, S. R. Marder, *Journal of the American Chemical Society* **2020**, *142*, 18637.
- [36] C. H. Feriante, S. Jhulki, A. M. Evans, R. R. Dasari, K. Slicker, W. R. Dichtel, S. R. Marder, *Advanced Materials* **2020**, *32*, 1905776.
- [37] C. M. Alder, J. D. Hayler, R. K. Henderson, A. M. Redman, L. Shukla, L. E. Shuster, H. F. Sneddon, *Green Chemistry* **2016**, *18*, 3879.
- [38] W. Ji, D. M. Kim, B. M. Posson, K. J. Carlson, A. C.

- Chew, A. J. Chew, M. Hossain, A. F. Mojica, S. M. Ottoes, D. V. Tran, et al., *RSC advances* **2023**, *13*, 14484.
- [39] D. M. Fischbach, G. Rhoades, C. Espy, F. Goldberg, B. J. Smith, *Chemical Communications* **2019**, *55*, 3594.
- [40] C. Krishnaraj, H. S. Jena, K. S. Rawat, J. Schmidt, K. Leus, V. Van Speybroeck, P. Van Der Voort, *ACS Applied Materials & Interfaces* **2022**, *14*, 50923.
- [41] D. Zhu, R. Verduzco, *ACS applied materials interfaces* **2020**, *12*, 33121.
- [42] W. Zhao, P. Yan, B. Li, M. Bahri, L. Liu, X. Zhou, R. Clowes, N. D. Browning, Y. Wu, J. W. Ward, *Journal of the American Chemical Society* **2022**, *144*, 9902.
- [43] M. I. Severino, E. Gkaniatsou, F. Nouar, M. L. Pinto, C. Serre, *Faraday Discussions* **2021**, *231*, 326.

Entry for the Table of Contents



Fifteen imine-linked covalent organic frameworks were synthesized in hours in the same mixture of n -butanol, water and acetic acid while stirring. The method is convenient, green, tolerates a wide variety of monomers, and can produce over ten grams of covalent organic framework in one batch.