Impact of Synthetic Parameters on the Size and Morphology of COF-300

Mohammad Izad Panah Ostad[1,*], **Balkaran Singh Sran** [1], **Laura M. Salonen**[1]

(1) CINBIO, University of Vigo, Department of Organic Chemistry, Vigo 36310, Spain

VIII ANNUAL MEETING CINBIO

Vigo, 10th & 11th of July 2025

Introduction

Three-dimensional covalent organic frameworks (3D COFs) have recently garnered significant attention due to their highly ordered structures, inherent porosity, and outstanding thermal and chemical stability. Their interconnected channels and high surface area make them ideal candidates for applications such as energy storage, gas adsorption and separation, heterogeneous catalysis, and targeted drug delivery .Since the size and morphology of COFs can play a critical role in determining their performance by affecting factors such as surface accessibility, mass transport, and interaction with guest molecules, it is important to understand how synthetic conditions influence these structural features.

In this study, we focused on exploring the influence of synthesis conditions on the size and morphology of COF-300, a well-known 3D COF, with the aim of retaining its crystallinity and high surface area. We systematically investigated the influence of key synthetic parameters, including solvents, reaction time, and temperature, on the resulting COF morphology and structural order. By employing an imine exchange strategy under mild conditions, we achieved a significant reduction in particle size (from approximately 1 μm to below 500 nm) within a shorter reaction time, while preserving the structural integrity and crystallinity of the framework.

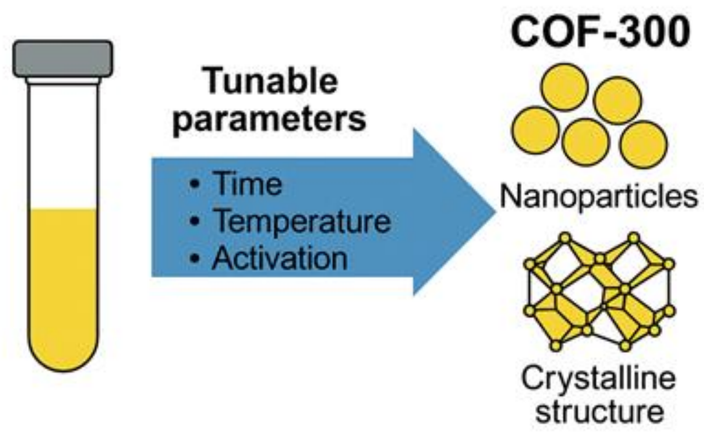

Figure 1. Solvothermal synthesis of COF-300 nanoparticles

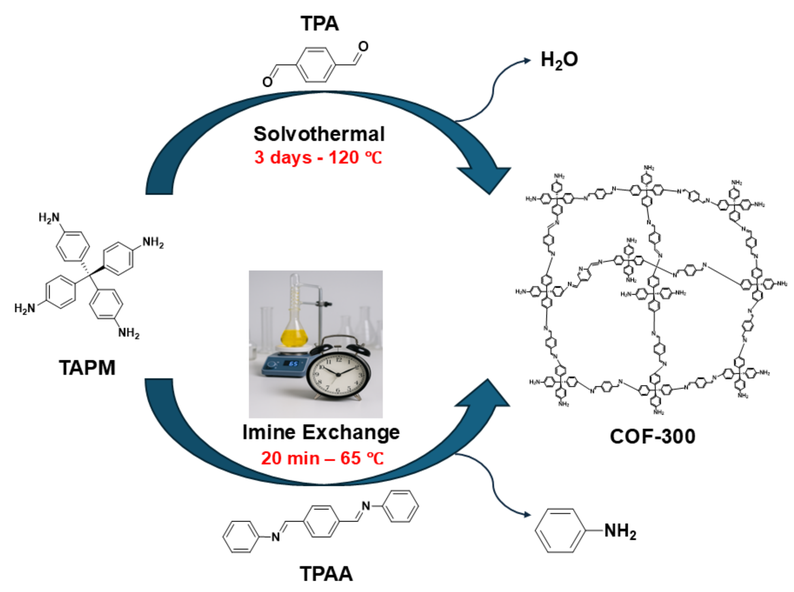

Figure 2. Comparison of two approaches for COF-300 synthesis using solvothermal and imine exchange method

To explore more efficient synthesis routes for COF-300, the study began with a conventional solvothermal method. Tetra-(4-anilyl)-methane and terephthalaldehyde, the building blocks of COF-300, were dissolved in 1,4-dioxane, followed by the addition of 3 M acetic acid as the catalyst, and the reaction mixture was heated at 120 °C for 3 days. The synthesized COF-300 material exhibited good crystallinity (Figure 3), consistent with previous reports in the literature [1,2]. Particle size analysis revealed that the synthesized particles were approximately 1 μm in size.

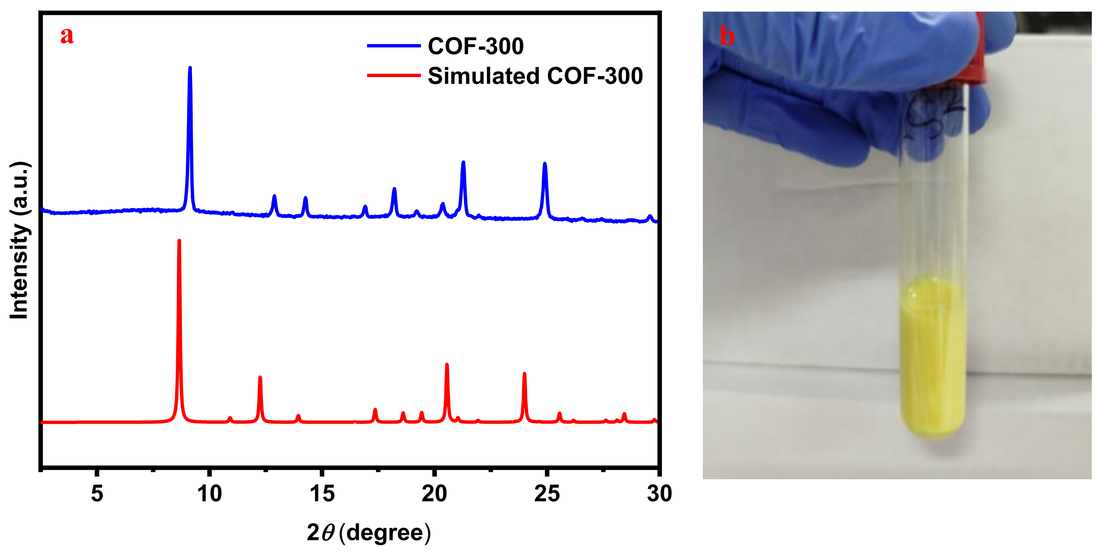

Figure 3. (a) Powder X-ray diffraction of COF-300 using solvothermal method. (b) The resulting COF-300 after 3 days of synthesis.

As an alternative to the conventional solvothermal method, an approach based on imine exchange chemistry was tested [3]. This strategy involved the prior condensation of terephthalaldehyde building block with aniline to give precursor *N*,*N*′-terephthalylidenedianiline (TPAA), the successful formation of which was confirmed by ^{1}H NMR spectroscopy. Conceptually, the imine exchange method relies on the reversible nature of the imine bonds, enabling self-correction of structural errors during the framework formation process. This dynamic behavior facilitates the assembly of highly crystalline structures under milder conditions and within a significantly shorter reaction time. Using this approach, COF-300 was synthesized using THF as solvent by refluxing at 65 °C in only 20 min, representing a remarkable improvement over the conventional method. Furthermore, this strategy reduced the particle size from approximately 1 μm to below 500 nm, while maintaining the framework's crystallinity.

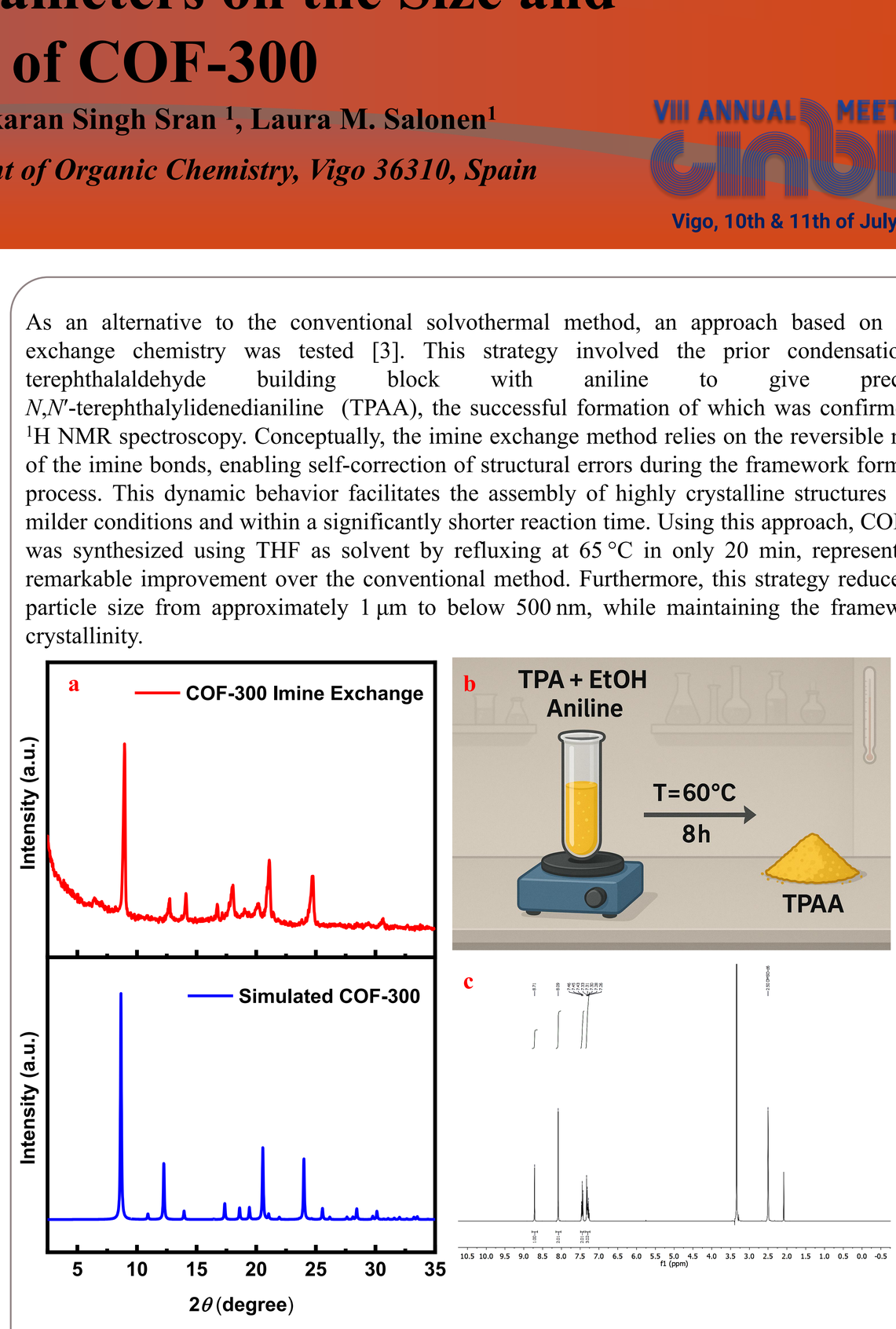

Figure 4. (a) PXRD of COF-300 synthesized using Imine exchanged method, (b) synthesis and (c) ^{1}H NMR of TPAA.

As shown in the TEM images, imine exchange synthesis significantly reduces the particle size of COF-300, reaching below 500 nm. In contrast, the particles synthesized via solvothermal method exhibit sizes around 1 μm (Fig 5 (a)) [1]. These results highlight the critical role of the synthesis conditions in achieving nanoscale control over particle morphology.

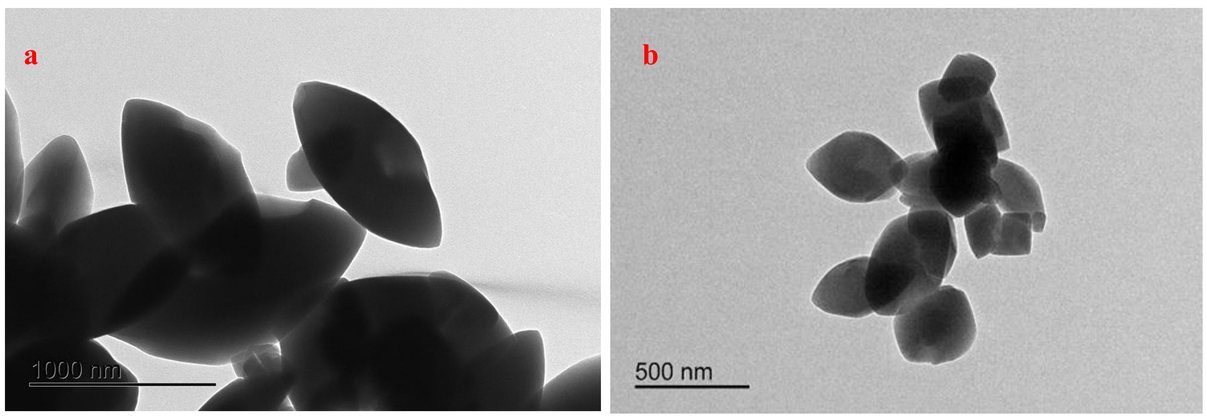

Figure 5. TEM images of COF-300 synthesized via solvothermal (a) and imine exchange method (b).

References

[1]. Fernando J. Uribe-Romo, Joseph R. Hunt, Hiroyasu Furukawa, Cornelius Klöck, Michael O'Keeffe, and Omar M. Yaghi, Journal of the American Chemical Society 2009 131 (13), 4570-4571.

[2]. Tong Liu, Yi Zhao, Min Song, Xinghan Pang, Xiaofei Shi, Jingjing Jia, Lifeng Chi, and Guang LuJournal of the American Chemical Society 2023 145 (4), 2544-2552.

[3]. Wang, X. L., Zhang, L. T., He, S., Chen, X. X., Huang, X. C., & Zhou, H. L. (2023). Dynamic Imine Exchange Reactions for Facile Synthesis of Imine-Linked Covalent Organic Frameworks. Chemistry of Materials, 35(23), 10070-10077.

Acknowledgement

LMS acknowledges financial support through the Ramón y Cajal grant RYC2020-030414-I funded by MICIU/AEI/10.13039/501100011033 and by"ESF Investing in your future".

This work was supported by the European Union's The European Innovation Council (EIC) program through the MemCat Project under grant agreement no. 101130047.

Disclaimer: Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or EIC and SMEs Executive Agency (EISMEA). Neither the European Union nor the granting authority can be held responsible for them.

European Innovation Council — Funded by the European Union — MEMCAT

Email: mohammad.izadpanah@uvigo.gal