

Synthesis of High-Performance Covalent Organic Frameworks via a Green Hydrothermal Route

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Humankind has a growing demand for advanced technologies and hence high-performance materials (HPMs), used in hi-tech devices. Yet, HPM syntheses are to date mostly harmful to the environment and human health, energy-intensive, and require solvents derived from petrol, which is a depleting resource. Clearly, green HPM syntheses are needed. One way to develop green and innovative pathways to HPMs is to take inspiration from chemical processes in nature. We recently developed a novel and green route for synthesizing heterocycle-linked organic HPMs, using nothing but high-temperature water as reaction medium: hydrothermal polymerization (HTP)¹. HTP is a geomimetic approach inspired by the natural mineral formation process “*hydrothermal crystallization*”, by which highly crystalline networks such as quartz form within hydrothermal veins. As its natural counterpart, HTP generates high crystallinity in organic materials².

Covalent organic frameworks (COFs) are an emerging class of crystalline organic materials, featuring periodic and homogenous pores, large surface areas, and low densities. Unfortunately, the majority of COFs reported to date disintegrate relatively easily under hydrolytic strain. Therefore, high-performance COFs linked by strong heterocyclic functions have recently attracted considerable interest.³ However, the latter are hard to obtain: generating crystallinity in COFs requires rendering the linking functions reversible under reaction conditions for correcting errors arising from kinetic attachment. Clearly, heterocyclic functions are hardly reversible. As we have shown that crystalline heterocycle-linked organic materials can be obtained hydrothermally,² we believe that HTP bears unique potential for generating high-performance COFs. With this contribution, we explore the formation of COFs via HTP including the discussion of a thorough set of characterizations of the obtained HPMs by various techniques.

Supported by the Austrian Science Fund (FWF) under the Grant “HYDROCOF – The hydrothermal route to covalent organic frameworks” (START Y1037-N28)

¹ B. Baumgartner et. al, *Polymer Chemistry* **2014**, 5, 3771. DOI: 10.1039/C4PY00263F

² M. M. Unterlass, *Angew. Chem. Int. Ed.* **2018**, 57, 2292. DOI: 10.1002/anie.201713359

³ C. R. DeBlase et. al, *Macromolecules* **2016**, 49, 5297. DOI: 10.1021/acs.macromol.6b00891