Solvothermal Template-Induced Hierarchical Porosity in Covalent Organic Frameworks: A Pathway to Enhanced Diffusivity

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The rapid advancement of covalent organic frameworks (COFs) in recent years has firmly established them as a new class of molecularly precise and highly tuneable porous materials. However, compared to other porous materials, such as zeolites and metal-organic frameworks, the successful integration of hierarchical porosity into COFs remains largely unexplored. The challenge lies in identifying appropriate synthetic methods to introduce secondary pores without compromising the intrinsic structural porosity of COFs. In this study, we realize a template-induced synthetic methodology to facilitate the construction of hierarchically porous COFs (hCOFs). This novel approach utilizes commercially available zinc oxide nanoparticles as a hard template, enabling us to increase the total pore volume of a series of β-ketoenamine-linked COFs as well as an imine-based COF while preserving their surface areas. In addition to transmission electron microscopy and gas adsorption analyses, small-angle X-ray scattering and pulsed field gradient nuclear magnetic resonance techniques were employed to investigate the hierarchical porosity and diffusivity of guest molecules within hCOFs. Our study demonstrates that the hierarchically porous nature of hCOFs significantly reduces diffusion limitations, thus leading to simultaneous enhancements in adsorption capacity, diffusivity, and catalytic performance.

Under review.

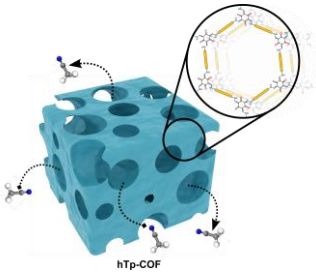

Figure 1: Schematic representation of hierarchically porous hCOF with acetonitrile diffusion.