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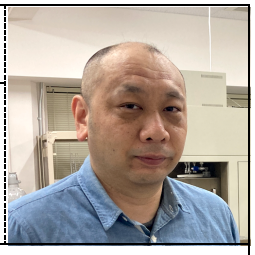

Exploring the Earliest and Latest Frontiers of PCP/MOF Science: From Flexible Gate Adsorption to 3D Inner-Crystal Mapping

Metal–organic frameworks (MOFs), with their tunable structures and defined porosity, have transformed adsorption science. This presentation explores both the *earliest* and *latest* frontiers of MOF research—tracing their evolution from fundamental discoveries to advanced functional design.

$[Co_2(4,4'\text{-bpy})_3(NO_3)_4]$ is one of the earliest PCPs, which displays gas adsorption with 1D channels. We describe a "squeezing adsorption" mechanism, where CO_2 molecules pass through seemingly closed windows via local ligand motion. A pressure-induced phase transition, driven by global lattice distortion, then leads to additional uptake. This dual-mode behavior reveals hidden structural dynamics even in the earliest PCP.[1)]

At the other end of the spectrum, we present 3D visualization of adsorption in MOF single crystals. Using in situ XAFS combined with Computed Tomography imaging, we mapped water adsorption in MOF-74-Co with 1 μm resolution. Adsorption initiates at the crystal core, not the surface, revealing clear spatial heterogeneity. Regions with high mosaicity show reduced uptake, highlighting the impact of local disorder—information inaccessible via traditional diffraction.[2)]

These two studies show that understanding both molecular-scale mechanisms and particle-level heterogeneity is vital for advancing MOF design. By bridging historical insight and modern imaging, we propose a framework for the development of next-generation porous materials.

1) Sakamoto, H.*, Otake, K.-i., Kitagawa, S.*, *Commun. Mater.*, **5**, 171 (2024).
2) Yamada, E., Sakamoto, H.*, Matsui, H., Uruga, T., Sugimoto, K., Ha, M.-Q., Dam, H.-C., Matsuda, R., Tada, M.*, *J. Am. Chem. Soc.*, **146**, 9181–9190 (2024).