Invited Lecture

Metal-organic frameworks with zero-valent metal nodes

J.N. McPherson[1], X. Liu[1], C.E. Andersen[1], K.S. Pedersen[1]

[1]Department of Chemistry, Technical University of Denmark, Kgs. Lyngby, Denmark

jnemc@kemi.dtu.dk

Despite the tremendous attention that has been paid to metal-organic frameworks (MOFs) over the last few decades, with very few exceptions [1-3], all have been constructed from anionic ligands and metal ions or clusters in moderate to high oxidation states. These structural motifs are vastly different to those encountered in organometallic chemistry and nanoparticle catalysis more generally. MOFs featuring zero-valent atoms or clusters are inherently more difficult to crystallize than conventional MOFs, due to the irreversibility and stricter directionality of the bonding, and so the impracticality of acquiring single crystals, large enough for even synchrotron facilities, has blockaded any development.

Electrons interact far more strongly with matter than X-rays, and so electron diffraction can be observed from crystallites that are orders of magnitude smaller than what has previously been required at single-crystal X-ray beamlines at synchrotron facilities (see **Figure 1**).

I will present how we have leveraged the recent availability of dedicated electron diffractometers to explore new framework architectures, for example featuring zero-valent metal atom and metal-clusters, that are beyond the limits of X-ray crystallography [2,3].

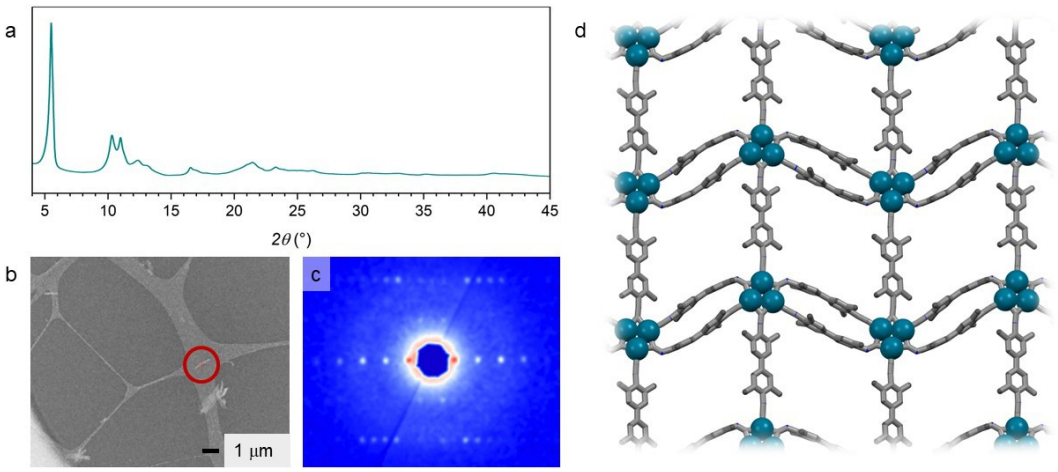

Figure 1. PXRD (1 = 1.5406 Å) of **Pd_3-MOF** (a). Real-space electron microscope image (b), unwarped (0*kl*) precession image (c) and the structure from continuous rotation 3D electron diffraction data of **Pd_3-MOF** [2].

[1] Sikma, R. E., Cohen, S. M (2022). *Angew. Chem. Int. Ed.* **61**, e202115454.

[2] Liu, X., McPherson, J.N., Andersen, C. E., Jørgensen, M. S. B., Larsen, R. W., Yutronkie, N. J., Wilhelm, F., Rogalev, A., Giménez-Marqués, M., Espallargas, G. M., Göb, C. R., Pedersen, K. S. (2024). *Nat. Commun.* **15**, 1177.

[3] Andersen. C. E., McPherson, J.N., Giménez-Marqués, M., Li, J., Kubus, M., Ito, S., Göb, C. R., Ott, S., Larsen, R. W., Espallargas, G. M., Pedersen, K. S. (2023). *J. Mater. Chem. C.* **11**, 11460.