Application Note

ELDIGO SCIENTIFIC
THE ELECTRON DIFFRACTION COMPANY

# Structure Determination of Nanocrystalline MOFs using ELECTRON DIFFRACTION

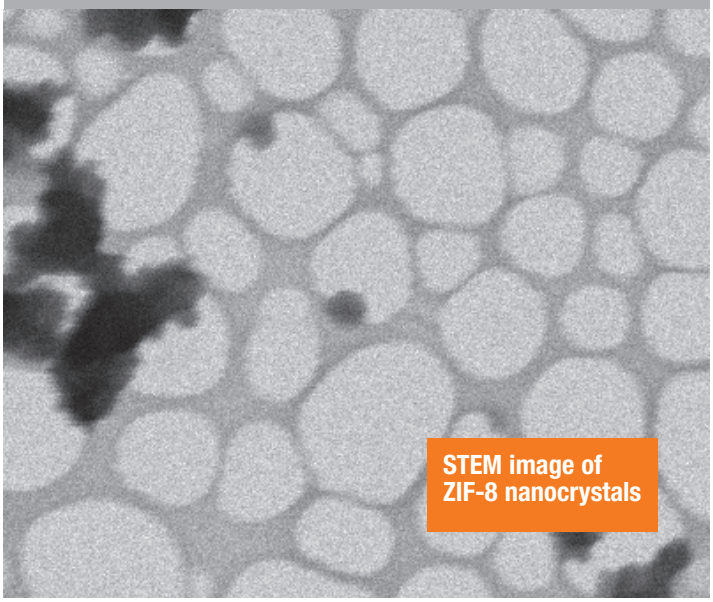
SHAPING THE FUTURE OF CRYSTALLOGRAPHY

As porous materials commonly prepared by solvothermal synthesis, MOFs often pose a challenge for traditional X-ray crystallography as their inherent properties do not allow for a recrystallisation, which makes structural analysis dependent on obtaining suitable single crystals straight from the synthesis. Being able to use nanocrystalline as synthesized material makes electron diffraction the perfect tool to tackle this problem and determine structures from crystals that are too small even for synchrotron facilities. In recent years, several novel MOF structures have been successfully determined by ED and it could also be shown that this is possible with high accuracy and even additional information can be extracted (e.g. about molecular motions, mixed-metal occupancies or interactions with guest molecules).[2]

## INHERENT MOF CHALLENGE: RECRYSTALLIZATION

Electron diffraction (ED, 3D-ED, MicroED) is gaining more and more momentum as a technique for the structural elucidation of challenging compounds as it bypasses the **main limitation** of growing crystals of suitable size for single-crystal X-ray diffraction. As such it has already found applications in all fields of research: from organic and inorganic compounds, over polymorphism, pharmacology, natural products, geological sciences, biomolecules, materials science to energy-storage materials and others.[1]

## EXPERIMENT ON ZIF-8



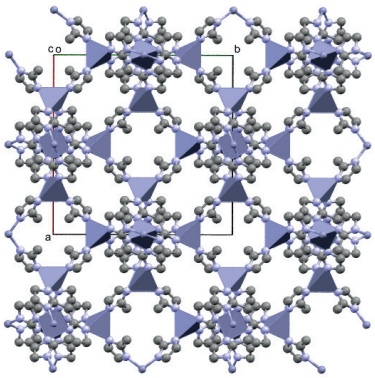
STEM image of ZIF-8 nanocrystals


[1] M. Gemmi, E. Mugnaioli, T. E. Gorelik, U. Kolb, L. Palatinus, P. Boullay, S. Hovmöller, J. P. Abrahams, ACS Cent. Sci. **2019**, 5, 1315-1329.

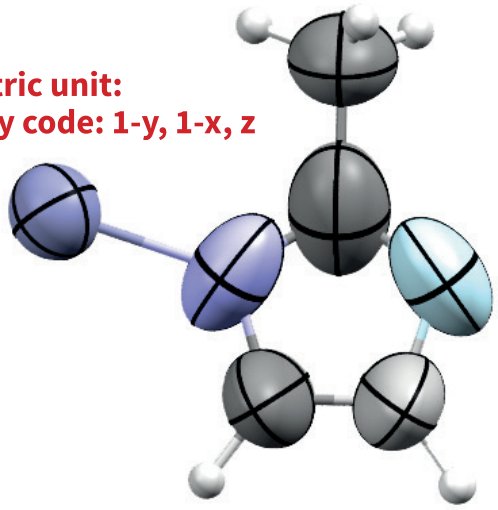
[2] Z. Huang, T. Willhammar, X. Zou, Chem. Sci. **2021**, 12, 1206-1219; Z. Huang, E. Grape, J. Li, A. K. Inge, X. Zou, Coord. Chem. Rev. **2021**, 427, 213583; L. Samperisi, A. Jaworski, G. Kaur, K. P. Lillerud, X. Zou, Z. Huang, J. Am. Chem. Soc. **2021**, 143, 17947-17952.

| CHEMICAL FORMULA | $C_8H_{10}N_4ZN$ |
|---|---|
| a = b = c (Å) | 16.94(18) |
| α = β = γ (°) | 90 |
| space group | $I\bar{4}3m$ |
| V (Å³) | 4859 |
| Independent reflections | 300 |
| Parameters | 34 |
| Restraints | 0 |
| Resolution (Å) | 1.2 |
| Completeness (%) | 97.7 |
| $R_{INT}$ (%) | 23.28 |
| $R_1$ [I > 2σ(I)] (%) | 12.71 |
| $wR_2$ [all data] (%) | 32.18 |
| Goodness of fit | 1.56 |

**Packing view**



**Asymmetric unit:**
**symmetry code: 1-y, 1-x, z**



## SET UP:

A nanocrystalline sample of ZIF-8 was finely dispersed on a standard TEM grid and measured on an ELDICO *ED-1* electron diffractometer. Suitable crystals were identified in STEM imaging mode. Further details on data collection can be found in **TABLE 1**. Data were processed and evaluated using the APEX4 soft ware package and implemented programs.[3] The frames were integrated and corrected for Lorentz effects, scan speed, background, and absorption using SAINT and SADABS. Space group determination based on systematic absences and E statistics was performed with XPREP. The structure was solved by SHELXD and refined with SHELXL in conjunction with ShelXle. Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were placed in calculated positions and refined with a riding model based on neutron diffraction distances and $U_{iso}(H) = 1.2 \cdot U_{eq}(C)$, methyl hydrogens were refined as part of rigid rotating groups and with $U_{iso}(H) = 1.5 \cdot U_{eq}(C)$.

| TEMPERATURE | AMBIENT |
|---|---|
| Electron energy | 160 keV |
| Wavelength | 0.02851 Å |
| Data collection method | single scan continuous rotation |
| φ range | -60° to 10° |
| φ increment | 0.5° per frame |
| Exposure time | 1 s per frame |
| Total measurement time | 140 s |


**The known structure of ZIF-8 was identified in a nanocrystalline sample.[4] Notably, a full anisotropic refinement of APDs could be performed without any restraints.**

## CONCLUSION

MOF samples which are nanocrystalline – either because larger crystals cannot be obtained or because applications require nano-sized particles – can readily be analyzed by electron diffraction. Dedicated instrumentation provides reliable data quality paired with easy operation, which will make ED accessible to a broader range of scientists in the future and thus establish it as an important part of the crystallographic toolkit, not only for MOFs.


[3] APEX suite of crystallographic software, APEX4 Version 2021.4-0, Bruker AXS Inc., Madison, Wisconsin, USA, 2021.

[4] K.S. Park, Z. Ni, A.P. Côté, J.Y. Choi, R. Huang, F.J. Uribe-Romo, H.K. Chae, M. O'Keeffe, O.M. Yaghi, Proc. Natl. Acad. Sci. U.S.A. **2006**, 10186-10191.