Electron Diffraction Analysis of a 3D Covalent Organic Framework

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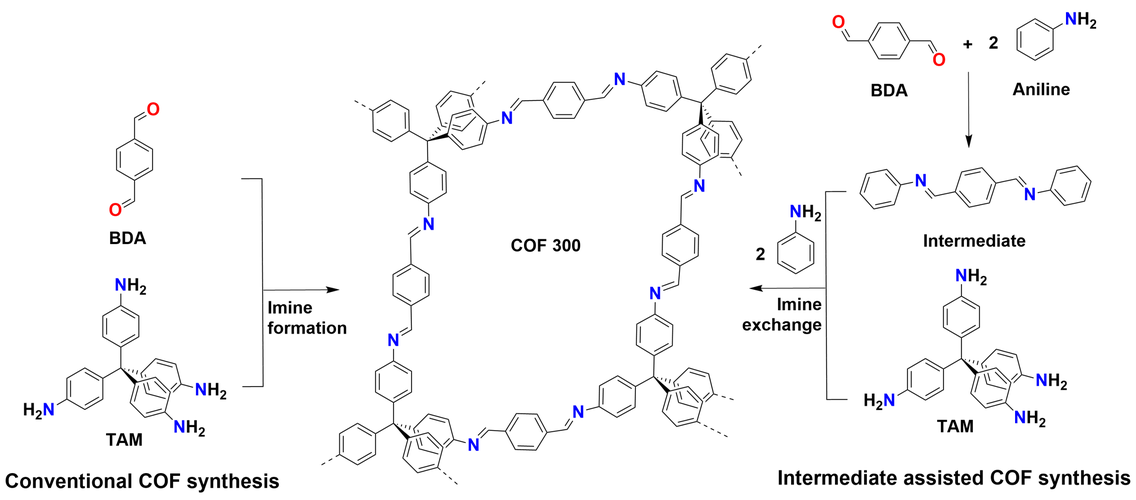
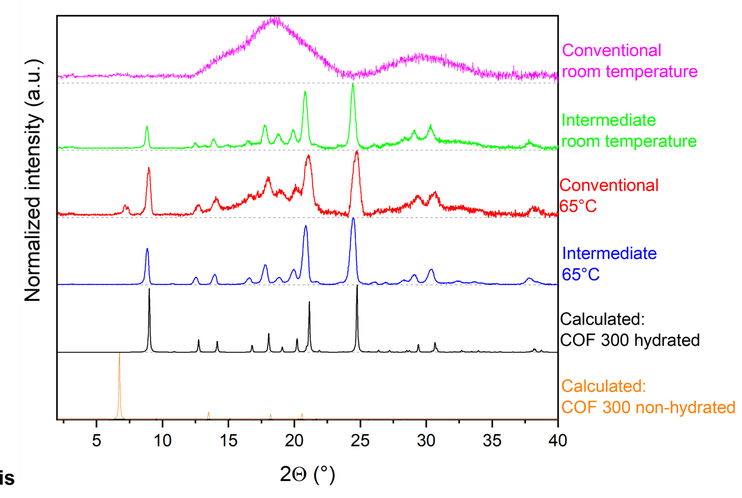
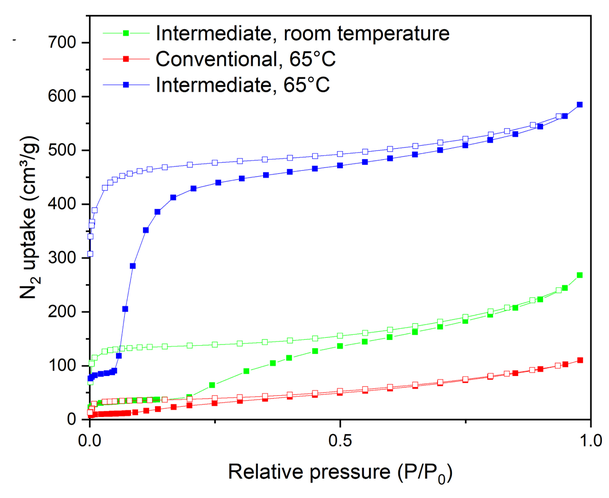
Introduction

Covalent Organic Frameworks (COFs) are attractive new materials due to their high designability. Numerous topologies, chemical functionalities and linkage types are reachable by careful selection of the used building blocks.[1] However, one major drawback is the limited crystallinity often observed in these materials due to the low reversibility of the employed strong covalent bonds. Reports of COFs suitable for single-crystal X-ray Diffraction analysis are very scarce and limited by the extensive reaction times necessary to reach large crystal sizes (>30 days).[2] Therefore, Electron Diffraction techniques are very attractive for these materials as even nanosized crystals can be readily analyzed.

Kinematical study





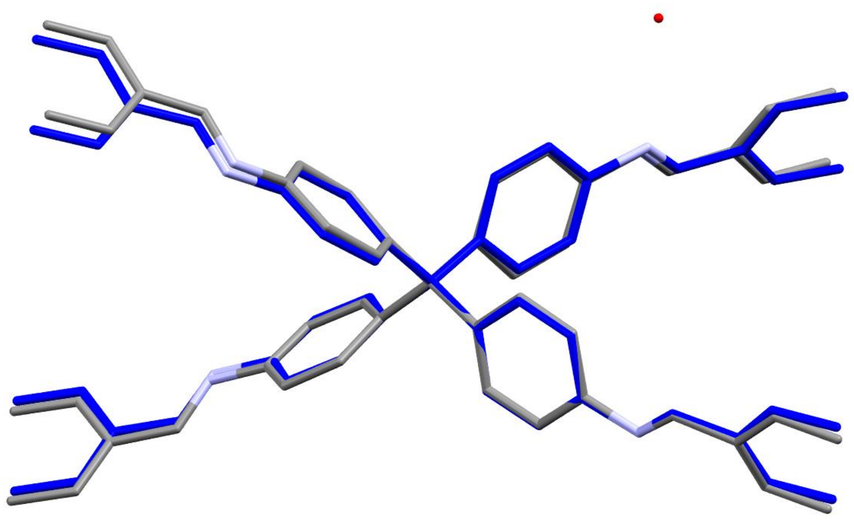


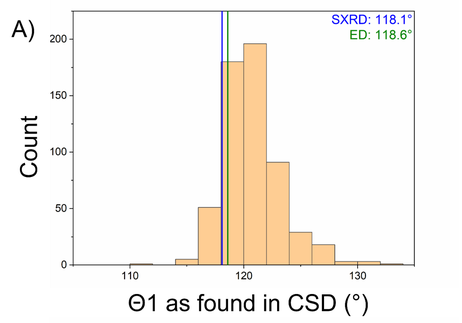
Using the developed intermediate assisted synthesis of COF-300, modulating aniline moieties are liberated *in-situ*, increasing the rate of error correction. This leads to faster crystallization (already after 6 h at 65°C instead of 1 d) and the possibility to synthesize crystalline COF-300 at room temperature.

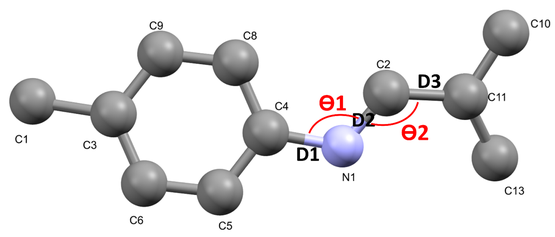
3D ED results

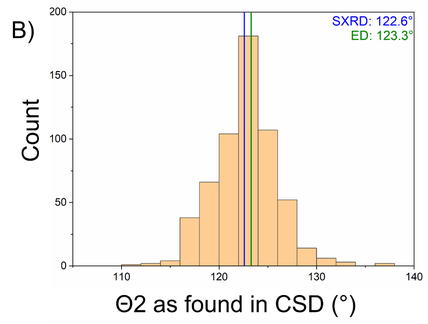
Rigaku XtaLAB Synergy-ED

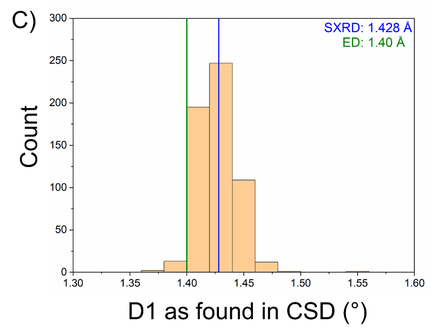
- JEOL 200 kV electron source with optics optimized for electron diffraction.
- Rigaku HyPix-ED detector optimized for operation in Micro-ED experimental setup.
- Sample stage allowing x,y,z sample alignment and rotation about a single axis with cryo option.

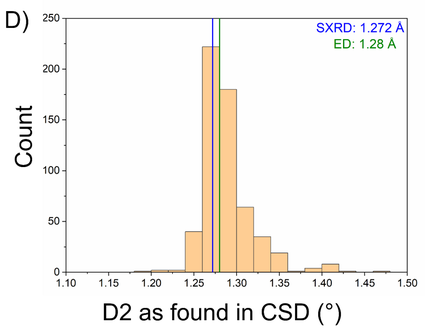


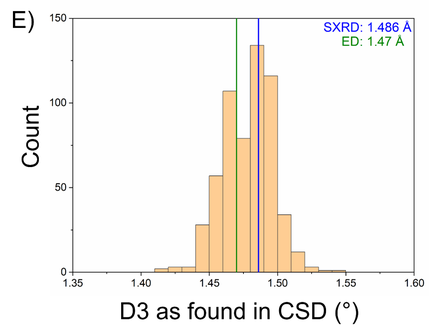




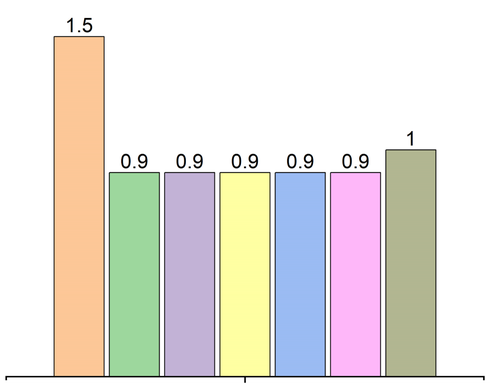


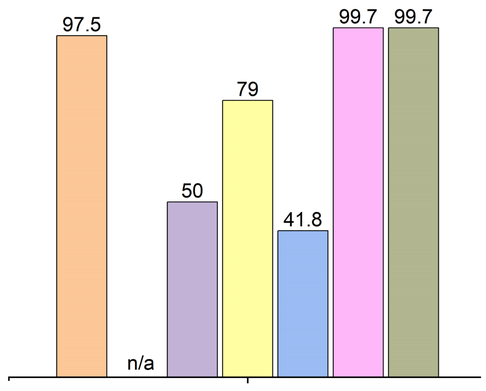


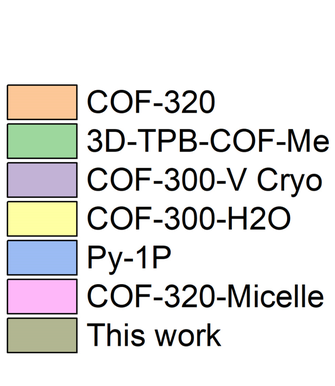


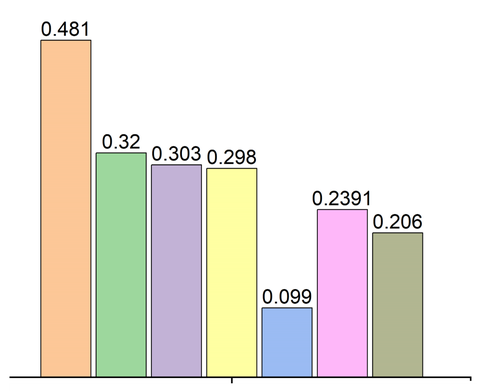


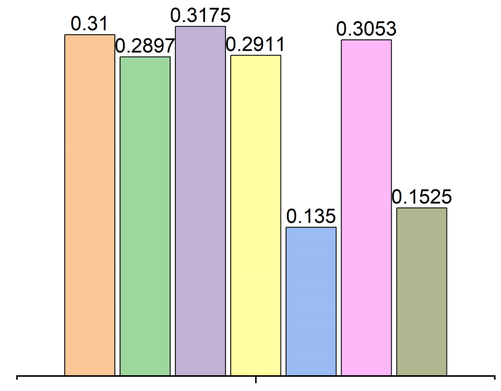
- The structure of the COF was solved via CrysAlis[Pro] and kinematically refined using ShelXL[3] via the Olex2 interface with **final R_1 value of 15.25%.** No additional restraints were employed but merohedral twinning of the data was observed (Twin Law: 0 1 0 | 1 0 0 | 0 0 -1; domain percentage: 84/16).
- Overlay of the obtained 3D ED structure (grey) and a reported SXRD structure[2] (blue) results in a very close match with a RMSD of 0.0282 Å.
- Zooming in on the formed imine connection shows realistic bond lengths and angles for both the 3D ED structure (green) and the reported SXRD structure[2] (blue) as compared to typical values found in the CSD.[4]
- Observed data statistics (resolution, completeness, R_{int} and R_1) where shown to be significantly improved compared to previously reported applications of ED on COFs.











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