Electron Diffraction Analysis of a 3D Covalent Organic Framework (COF-300)

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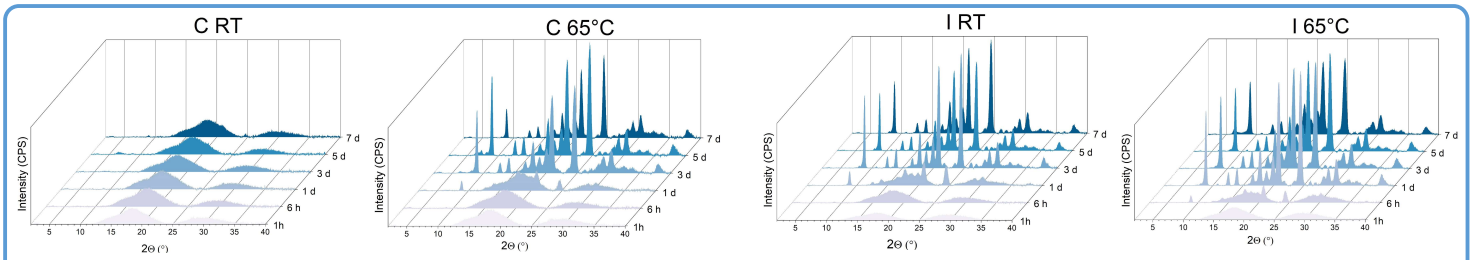
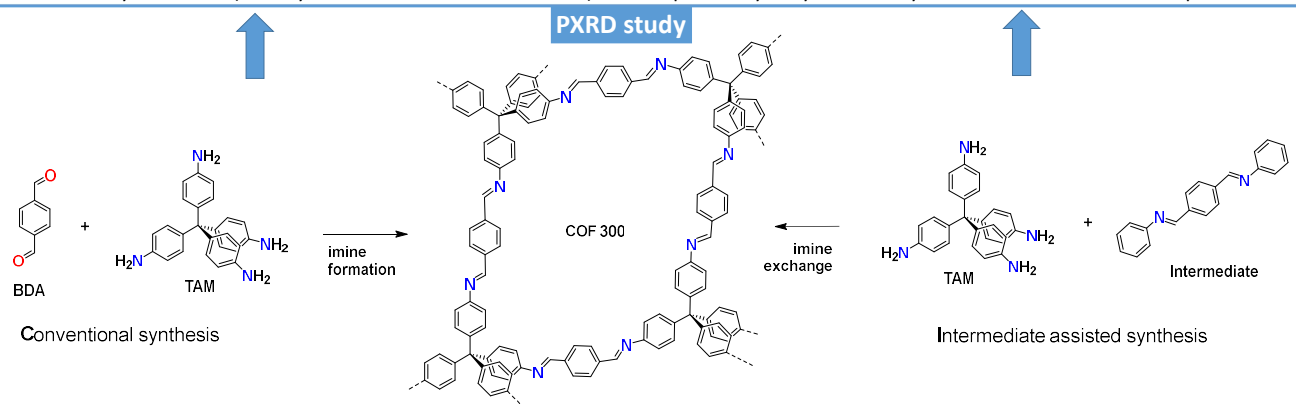
Introduction

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.



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.

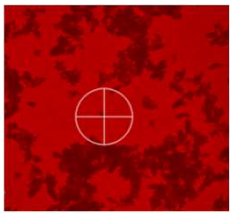
PXRD study



Electron Diffraction

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.



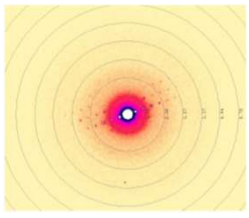
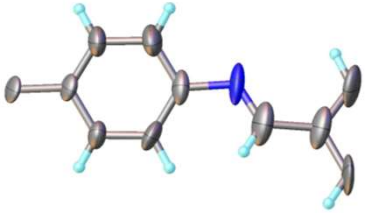
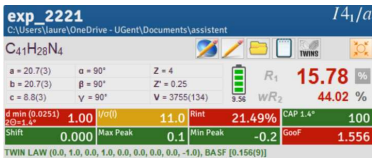


Table 1. Data statistics. All datasets were collected at room temperature, using wavelengths of 0.0251 Å, scan width of 0.5° and exposure time of 1 s. Data set 'Total' was obtained by merging of datasets 1 and 2. Point group symmetry: I 4/m

Set	# frames	Time (min)	Completeness (%)	Redundancy	$\langle F^2/\sigma(F^2)\rangle$	R_{int}	R_{pim}	R_{sigma}
1	180	3:10	99.7	3.5	7.65	0.155	0.098	0.173
2	200	3:30	89.4	4.2	10.98	0.165	0.088	0.180
Total			99.7	7.2	10.89	0.215	0.082	0.148





- The structure of the COF was solved via CrysAlis^{Pro} and kinematically refined using Olex2[3] with **R_{int} of 21.49% and R_1 value of 15.78%.** No additional restraints were employed but merohedral twinning of the data was observed (Twin Law: 0 1 0 | 1 0 0 | 0 0 -1).
- A dynamical refinement protocol is also being studied, with data processing via PETS2[4] and subsequent structure solution, kinematical and dynamical refinement using Jana2020. Currently, **R_{int} around 12% and R_{obs} of 15%** have been reached.
- Twinning of the COF seems problematic for the dynamical refinement with a high obtained R_{obs} value and the appearance of negative displacement parameters.

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[3] O. V. Dolomanov , L. J. Bourhis , R. J. Gildea , J. A. K. Howard and H. Puschmann , *J. Appl. Crystallogr.*, 2009, **42** , 339 —341
[4] L. Palatinus, P. Brázda, M. Jelínek, J. Hrdá, G. Steciuk and M. Klementová, *Acta Cryst. B,* 2019, **75**, 512-522.

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