Crystal structure determination of nanocrystalline organic compounds – pushing the limits

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Crystal structure determination from powder diffraction data consists of three steps: (1) indexing, i.e. determination of lattice parameters and space group; (2) structure solution (for organic compounds usually with direct-space methods, using of the molecular geometry); (3) Rietveld refinement.
For nanocrystalline compounds with powder patterns containing only 10-20 broad 'peaks', the indexing becomes challenging or even impossible. If indexing fails, the lattice parameters remain obscure, and only a few methods can be applied.

(1) Recrystallisation with the aim to obtain a better crystalline, phase-pure powder
(2) Intuition, model building or isotypy with a known structure
(3) Crystal structure prediction using force fields or quantum mechanical methods
(4) Electron diffraction (However, even electron diffraction requires a minimum level of crystallinity. For organic compounds the minimum required domain size is currently approximately 30 nm [1])
(5) Global fit to the powder data without prior knowledge of lattice parameters and space group, starting from a large set of random structures in different space groups with random values for the lattice parameters ('FIDEL fit') [2]
(6) Global fit to the pair-distribution function, starting from a large set of random structures ('Global PDF fit') [3,4], see Figure 1.

In the presentation, all methods shall be explained, their limitations are discussed, and examples for their application to nanocrystalline organic compounds shall be given.

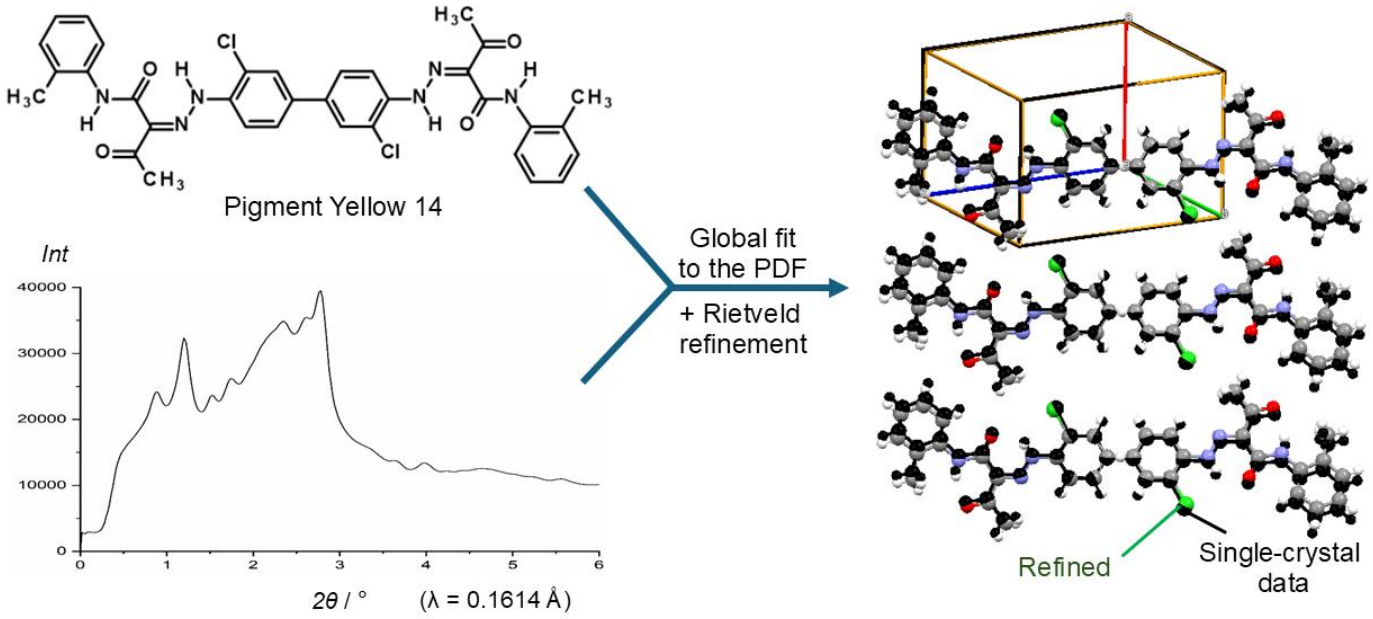


Figure 1. *Crystal structure determination of a nanocrystalline organic sample with a domain size of only 10 nm, using a global fit to the pair-distribution function.*

[1] M.U. Piepenbring, A. Winderling, T. Gorelik, submitted.
[2] S. Habermehl, C. Schlesinger, M.U. Schmidt, Acta Cryst. (2022), B78, 195–213.
[3] C. Schlesinger, S. Habermehl, D. Prill, J. Appl. Cryst. (2021), 54, 776–786.
[4] R. Huehn, J. Elsaß, S. Habermehl, M.U. Piepenbring, submitted.