Poster

High temperature electron diffraction on organic crystals: *in situ* crystal structure determination of Pigment Orange 34

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Small molecule structures and their applications rely on a good knowledge of their atomic arrangements. However, the crystal structure of these compounds and materials, which are often composed of fine crystalline domains, cannot be determined with single-crystal X-ray diffraction. Three-dimensional electron diffraction (3D ED) is already becoming a reliable method for the structure analysis of submicron-sized organic materials[1]. The reduction of electron beam damage is essential for successful structure determination and often prevents the analysis of organic materials at room temperature, not to mention high temperature studies.

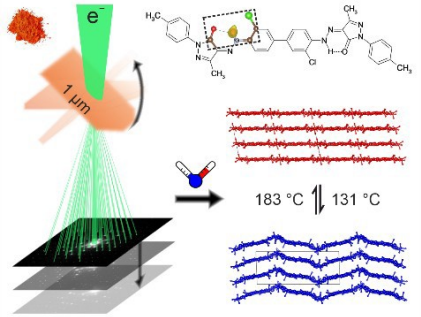

Figure 1. Electron diffraction at 220 °C was necessary to structurally elucidate the reversible phase transition of the fine crystalline industrial organic Pigment Orange 34.

In this work, we apply advanced 3D ED methods at different temperatures enabling the accurate structure determination of two phases of Pigment Orange 34 ($C_{34}H_{28}N_8O_2C_{l2}$), a biphenyl pyrazolone pigment that has been industrially produced for more than 80 years and used for plastics application[2]. The crystal structure of the high-temperature phase, which can be formed during plastics colouration, was determined at 220 °C. For the first time, we were able to observe a reversible phase transition in an industrial organic pigment in the solid state, even with atomic resolution, despite crystallites are submicron in size. By localising hydrogen atoms, we were even able to detect the tautomeric state (see Fig. 1) of the molecules at different temperatures – although the structure contains 148 symmetrically independent atoms.

This demonstrates that precise, fast and low-dose 3D ED measurements enable high-temperature studies of organic materials, opening the door for general in situ studies of nanocrystalline materials at atomic level.

[1] P. B. Klar, Y. Krysiak, H. Xu, G. Steciuk, J. Cho, X. Zou, L. Palatinus, *Nat. Chem.* **2023**, *15*, 848–855.

[2] Y. Krysiak, S. Plana-Ruiz, L. Fink, E. Alig, U. Bahnmüller, U. Kolb, M. U. Schmidt, *J. Am. Chem. Soc.* **2024**, *146*, 9880–9887.