Invited Lecture

Polymorphism of thin molecular crystals

P. Brázda

[1]*Institute of Physics of the Czech Academy of Sciences, Na Slovance 1999/2, 18200 Prague 8, Czechia*

brazda@fzu.cz

Different packing of molecules in crystals leads to different properties of solids. 3D electron diffraction (3D ED) has been successfully used in two different research projects where the determination of the structure was crucial to explain the observed properties of the prepared materials: (a) nanocrystals blooming on fibers used to fabricate long-lasting bed nets for malaria control (Figure 1) and (b) nanocrystals showing cooperative phase transitions.

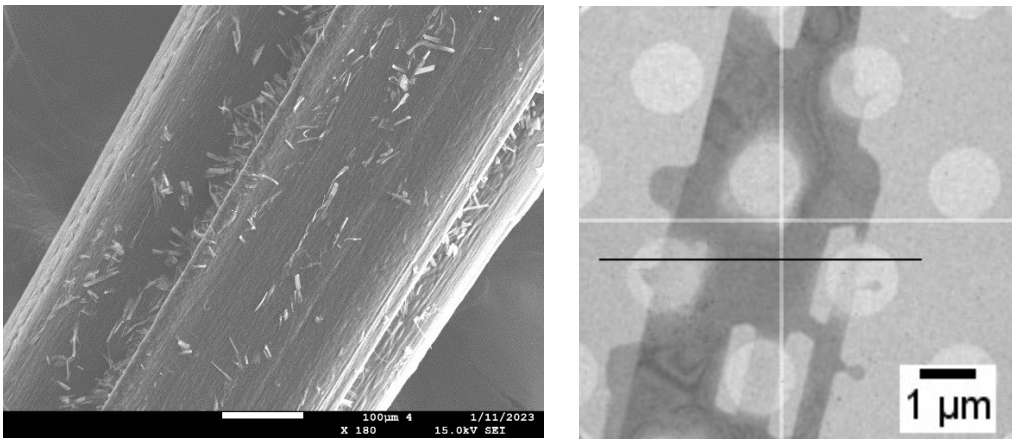

Figure 1. Chlorfenapyr insecticide nanocrystals bloomed on a polyethylene fiber. SEM image (left), nanocrystal on TEM grid. Crystal thickness was comparable to the thickness of the carbon foil (about 20 nm).

Ad (a): The role of polymorphism in the action of pesticides and insecticides has become evident only recently [1]. An inverse correlation between lethality of contact insecticides and thermodynamic stability of crystal polymorph has been found in several contact insecticides, including DDT, lindane, deltamethrin, and imidacloprid. The use of a more lethal polymorph of a contact insecticide can overcome resistant organisms. Greater efficiency requires the application of less active ingredient, reducing the environmental impact. Given the increasing importance of polymorphism in the activity of contact insecticides, it is surprising that there is no information in the literature about the solid states of chlorfenapyr. Our results results filled this gap – we were able to solve four different chlorfenapyr polymorphs, two of them were determined solely by the 3D ED and one was solved independently by synchrotron SCXRD and 3D ED.

Ad (b) Cooperative phase transitions are diffusionless and reversible phase transitions caused by a concerted displacement of molecules, atoms, and ions in crystals. They are generally associated with interesting macroscopic phenomena, such as the tuning of the mechanical properties of the materials undergoing the transition and shape-shifting effects, and they have been extensively studied in metals, inorganic alloys and ceramics. Reports on cooperative polymorphic transitions of molecular crystals are still rare and the molecular mechanisms underlying these peculiar transformations are still largely unknown. We studied crystals of C6-BTBT molecule, which should have only one polymorph at temperatures below 300 K. Using powder XRD and 3D ED we revealed and solved the structure of at least three other polymorphs and were able to describe the mechanism behind the polymorphic transitions.

[1] Erriah, B. et al., (2022) *Insects,* **13**, 292.

[2] Aronin, R., et al., (2024) *Cryst. Growth Des*., **24**, 1284.

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