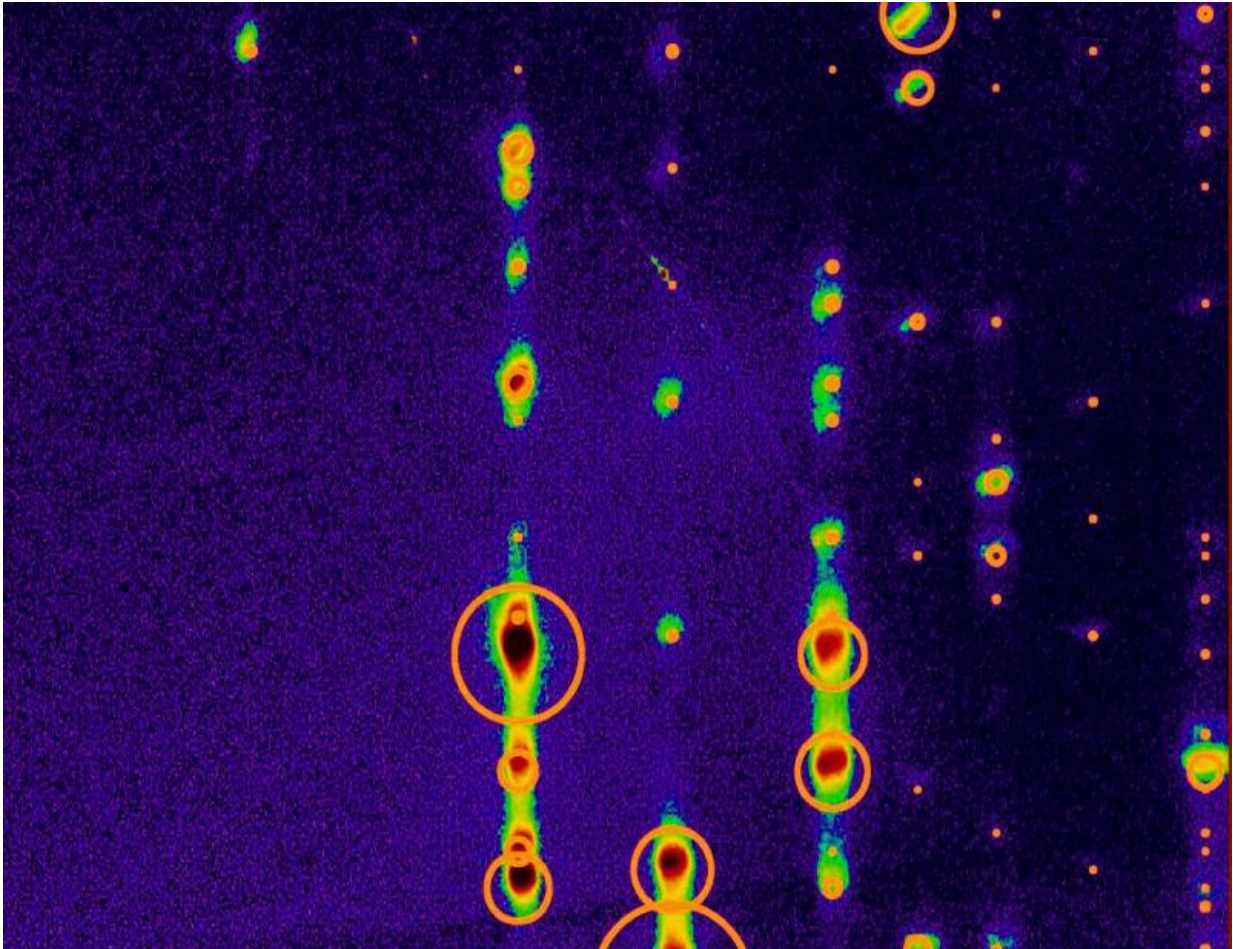


Doped organic semiconductors explored

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X-ray diffraction on pure 4T, colored for christmas reasons. Credit: HZB

Current semiconductor technology is based on silicon, an inorganic semiconductor material in which impurity atoms are introduced or

doped for use in electronic components to increase conductivity and tailor the electronic structure. However, organic solid-state materials made of conjugated molecules or polymers can also exhibit promising semiconducting properties that make their application feasible for organic electronics.

Guest molecules in a host structure

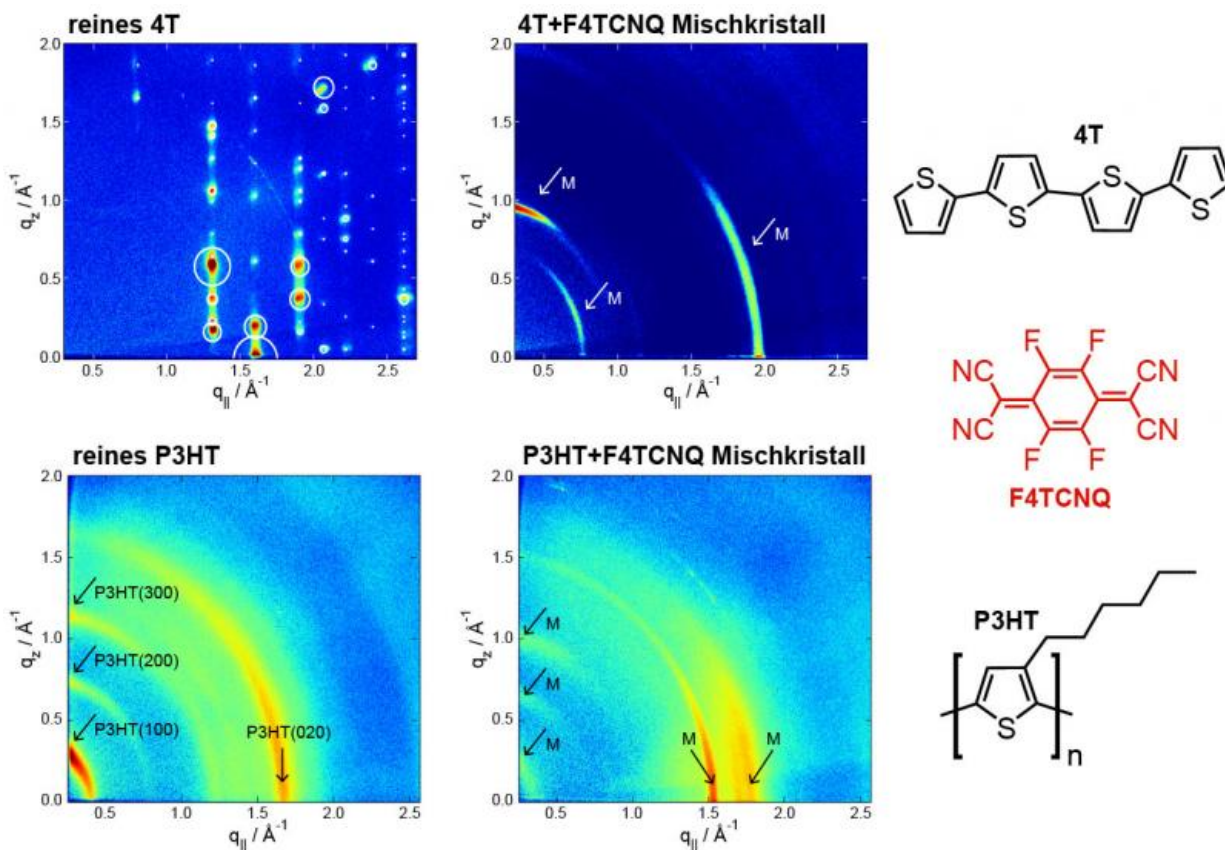
The enormous application potential of [organic electronics](#) has been clearly demonstrated for example by the success of organic LEDs (OLEDs) in the recent years. Oligothiophene (4T) and polythiophene (P3HT), two typical organic semiconductors, can be doped with a second type of molecule such as a strong electron acceptor (F4TCNQ) for example to control the electrical conductivity. However, until recently, how these guest molecules are exactly integrated into the host structure was poorly understood. A homogenous distribution analogous to that in inorganic semiconductors had therefore always been assumed.

Unusual characteristics

An international group headed by the Molecular Systems Joint Research Team at the HZB and Humboldt-Universität zu Berlin has now been able to demonstrate that this is not the case for either oligothiophene or polythiophene. The group, co-led by Dr. Ingo Salzmann and Prof. Norbert Koch, had previously experimented with and already modelled other systems to learn how doping organic semiconductors affects their electronic structure and thus their conductivity. This produced clues about unusual characteristics of this class of materials in which hybridisation of the molecular orbitals plays a key role.

They therefore fabricated a series of organic thin films with increasingly heavy levels of doping and investigated these samples using X-ray

diffraction techniques at the KMC-2 beamline managed by Dr. Daniel Toebeens. They were able to precisely determine the dependence of the crystalline structure on the degree of doping using this technique.



Left, X-ray scattering reveals characteristic reflections of the pristine host lattices for 4T (top) and P3HT (bottom). In the case of heavily doped materials (right column), fundamentally different reflections occur that provide evidence for the presence of co-crystallites formed by dopant and host. Credit: HZB

Co-crystallites as dopants

Their results for the organic semiconductors 4T and P3HT showed that

the guest molecules - quite contrary to the expectations - are not uniformly incorporated in the host lattice at all. Instead, a second crystalline phase of host/guest co-crystallites is formed in the pure crystalline host matrix. These co-crystals function in the role of dopant in place of the actual, pure doping molecules in such systems.

Better understanding for more control

"It is important to understand the fundamental processes involved in the molecular electrical doping of organic semiconductors more precisely", explains Salzmann, continuing: "If we want to successfully employ these kinds of materials in applications, we need to be able to control their electronic properties just as precisely as we customarily do today with inorganic semiconductors".

More information: Henry Méndez et al. Charge-transfer crystallites as molecular electrical dopants, *Nature Communications* (2015). [DOI: 10.1038/ncomms9560](https://doi.org/10.1038/ncomms9560)

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