

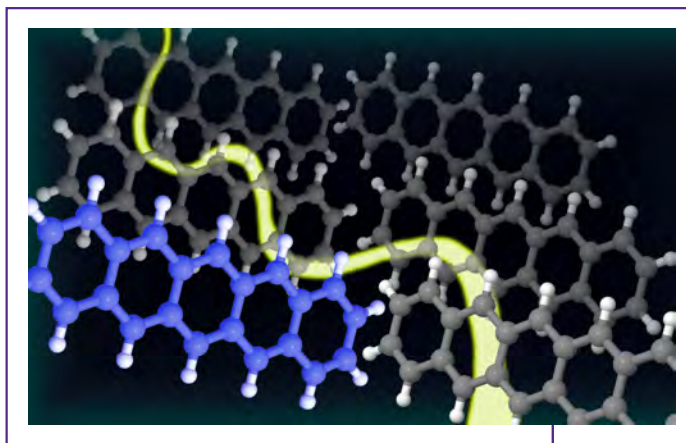
Electrons go green: Exploring organic semiconductors

Smartphones, large-size TV screens or bendable lamps: applications of OLEDs - Organic Light Emitting Diodes – are proliferating rapidly and demonstrate strikingly how fundamental research bears fruit in everyday life. These are prominent examples of the developing class of organic semiconductor devices. The latter consist of polymers or organic molecules, i.e. they are based on carbon and hydrogen instead of traditional materials like silicon. This brings convincing advantages: the end products -ranging from OLEDs to organic electronic devices- are light, flexible and environment-friendly.

Combining two worlds: Besides these promising applications, organic semiconductors are also highly interesting from a fundamental point of view. On the one hand, standard inorganic semiconductor materials are well understood and solid state physics theory provides precise models to predict their properties. On the other hand, theoretical chemistry describes the features of isolated molecules very well. Organic semiconductors lie in between these two worlds and the exact microscopic mechanisms governing their electronic properties are still open questions. These materials form crystals where, instead of atoms held together by strong covalent bonds, we have weakly connected molecules. When only the standard methods of either physics or chemistry are applied, experimental results cannot be reproduced theoretically. This limits our current understanding of organic compounds and new approaches have to be found, combining the insights of both sciences. This was the aim of recent work carried out by Institut NEEL researchers working with colleagues based in Italy, Denmark and the USA.

The experimental challenge : In this work, the electronic band structure of pentacene crystals was measured accurately using Angular-Resolved Photoemission Spectroscopy (ARPES). Pentacene is a small and rather simple molecule, and the pentacene crystal (Fig. 1) constitutes a typical case-study for organic semiconductors in general. We focused on the band structure, because it is an indispensable feature, directly related to fundamental material properties such as the conductivity and optical absorption. The band structure is like a map, indicating which values of energy and momentum an electron can possess within the crystal. The ARPES technique has been much used to measure the band structure of inorganic materials, but precise measurements for organics have only become possible during the last five years. One reason is the weak binding of the molecules, which easily evaporate under ultraviolet radiation. Moreover, it is extremely difficult to grow a perfectly periodic organic crystal – a necessary condition to obtain satisfying ARPES signals. Our collaborators succeeded in drastically improving the experimental resolution, and also reduced the molecular disorder by optimizing the sample preparation.

A challenge for theory: Determining the band structure from theory is even more challenging. Since the molecules are held together by rather weak forces- in contrast to atoms in a crystal- they mostly retain their molecular identity, but available standard band structure theories have been developed for atomic crystals. In those theories, the electrons move freely in the crystal instead of belonging to a specific atom. This is a valid description for inorganic atomic crystals, but the molecular aspect is completely missing. We demonstrated this by using one of the most accurate band structure theories and comparing the results to the



measured high-resolution pentacene band structure. The disagreement between experiment and theory was obvious. The question then was: Which molecular properties are missing in the standard theoretical approach?

From molecules to crystals: A hint could be found in past Photoemission Spectroscopy experiments performed on free organic molecules in the gas phase, which showed that the molecular vibrations, i.e. the periodic oscillations of their constituent atoms, completely reshuffle the available electronic energies in the molecules: a characteristic "shakeoff" spectrum appears, which is a hallmark of the strong interconnection between the electrons and vibrations. We therefore calculated the strength of this effect, the so-called electron - molecular vibration (EMV) coupling, for a single molecule and combined it with a crystal band structure calculation, to describe simultaneously the molecular (vibrational) and crystalline nature (band structure) of these materials. The resulting modified band structure shows coexisting features of the shakeoff spectra of individual molecules and of the usual bands of the crystalline solid, and is in extremely good agreement with the experimental measurements. Inclusion of the molecular ingredient was therefore crucial to explain the puzzling features observed in experiments.

Pentacene, more than a study case: Our combined experimental and theoretical study on pentacene has demonstrated unambiguously that fingerprints of the molecular constituents are clearly visible in the electronic energy spectrum. These features are now systematically being observed in experiments on several other organic molecular compounds, which suggests that the relevance of the present findings could extend well beyond the pentacene study-case presented here.

Artist's view of electronic transport (the green curve) in an organic crystal. The building blocks of the crystal are pentacene molecules (formula $C_{22}H_{14}$) consisting of five benzene rings linked together (e.g. the blue group in foreground). The molecules stack together in a loose, complex geometry to form the crystal.

CONTACT

Simone FRATINI
simone.fratini@neel.cnrs.fr

Ph.D STUDENT
Carina FABER

FURTHER READING

MOLECULAR FINGERPRINTS IN THE ELECTRONIC PROPERTIES OF CRYSTALLINE ORGANIC SEMICONDUCTORS: FROM EXPERIMENT TO THEORY
S. Ciuchi, R. C. Hatch, H. Höchst, C. Faber, X. Blase and S. Fratini
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