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At the source of chirality: Microscopy reveals details of self-assembly of liquid crystal dimers

Liquid crystal layers a single molecule thick can form extremely complicated structures. The complex construction of these monolayers makes it difficult to visualize them using standard scanning microscopy. Despite this, images from an STM, obtained at the Institute of Physical Chemistry of the Polish Academy of Sciences in Warsaw, reveal, for the first time, structural details of monolayers of liquid crystal dimers, also indicating the mechanisms responsible for the birth of chirality.

Molecules of liquid crystals aggregate into spatial structures that are often impressively complex. Under the appropriate conditions, however, they can be forced to cover a substrate with the thinnest layer possible, i.e. with the thickness of a single molecule. Due to the complex structure of the molecules themselves and the complicated manner in which they order themselves, even such monolayers remain thankless to modern scanning microscopes. Researchers from the Institute of Physical Chemistry of the Polish Academy of Sciences (IPC PAS) in Warsaw, assisted by researchers from the University of Warsaw, Warsaw University of Technology and the British University of Hull, have, however, overcome these difficulties posed by nature. The images obtained by means of a scanning tunneling microscope (STM) show, for the first time, details of the structure of monolayers formed by liquid crystal dimers and reveal the patterns forming on their surface.

The monolayers that were examined at the IPC PAS consisted of molecules built of two units (dimers). Depending on the type of liquid crystal tested, the dimers were connected by a spacer consisting of a sequence of 7 to 12 methylene (CH_2) groups. It has been known for a long time that the number of groups in the spacer has an interesting effect on the form (conformation) of molecules in the monolayer and its structure. When the number of carbon atoms is even, the particles have a z-shape, and the elementary cells of the liquid crystal formed from them do not exhibit chirality. However, when there is an odd number of carbon atoms in the spacer, the dimers bend into banana-like shapes. When forming elementary cells, the bent particles twist in relation to each other and the resulting two-dimensional crystal begins to show chirality.

“Chirality is usually inherited: if the molecules are chiral, so are the elementary cells of the crystal and the whole crystal that is built of them. But in some cases, both the cells and the crystals can be chiral despite the fact that molecules that form them are not. The images registered by us show the first stage of formation of this sort of chirality,” says Prof. Robert Nowakowski (IPC PAS).

In the case of liquid crystal monolayers, the interpretation of STM images becomes particularly difficult. In every elementary cell there are even a dozen or so mutually more or less entangled particles, each with a rich internal structure. Obstacles also appear with regard to the tunneling microscopy itself. The tunneling current that is measured here is the current between the end of the probe and the sample. Thus, the brighter spots in the image are not areas that reflect light better, but those that conduct current better. However, a number of factors influence current, including the number of conductive elements on the tested surface, as well as their electron properties. In interpreting the images, the researchers had to refer to the elementary cell model of the liquid crystal under study. The model obtained by means of X-ray diffraction came from the Cambridge Structural Data Base.

“The model of the elementary cell of one of the most interesting of the liquid crystals we examined, CB9CB, was a three-dimensional structure, formed of many layers, with long strings of particles twisting into helices. Meanwhile, we had only one layer. So we had to find its counterpart in the model – a plane in which the distribution of molecules was best correlated with the patterns of light and dark spots visible on the microscope images. This was how we determined that the single bright spots on our microscope images corresponded to the two paired cyanobiphenyl groups of adjacent molecules,” explains Prof. Nowakowski.

At the IPC PAS, images of monolayers of several dimers with different spacer lengths were taken. The dimer containing the shortest spacer (seven carbon atoms) was found to be particularly interesting. Essentially, these dimers formed ordered parallel rows of molecules oriented in one direction in the monolayer. An interesting observation, however, was that on a local scale they also organized into a clearly different structure, resembling an immobile four-bladed windmill shape. Its blades consisted of the differently oriented cyanobiphenyl groups of four adjacent molecules. Here, chirality was the consequence of the fact that these groups (the blades) lying in the plane of the monolayer did not converge in the centre of the “windmill”. Instead, each of them was attached to the adjacent blade at a certain distance from the axis of the “windmill”. This pattern of molecules can be levorotatory or dextrorotatory, and is therefore chiral.

The imaging of liquid crystal monolayers at the molecular level will help in a better understanding of the mechanisms of self-organization of these structures, and will also make it possible to determine the conditions of their formation more precisely. It is conceivable that, with time, we will be able to fully reveal the story behind the birth of supramolecular chirality, in particular the nuances of the earliest stages of the formation of helices in the elementary cells of a three-dimensional crystal.

The work on monolayers of liquid crystal dimers, funded by the OPUS grant from the Polish National Science Centre, is of a basic nature. However, it can be translated into practice due to the fact that modern nanotechnology often uses thin layers. The potential applications in optics, from the simplest in the form of polarizing filters to much more sophisticated ones, such as lasers with an electrically regulated wavelength, seem particularly interesting. In the latter devices, what is important is that the helices formed by the molecules of the active centre can, under the influence of an electric field, change their period of full rotation, which translates into a change in the length of light wave emitted by them (the shift is even 100 or more nanometres). In turn, the short optical response times of helices from achiral molecules, which are quite surprising in the case of such large structures, give hope for the construction of displays that are much faster than current ones.

The Institute of Physical Chemistry of the Polish Academy of Sciences (http://www.ichf.edu.pl/) was established in 1955 as one of the first chemical institutes of the PAS. The Institute's scientific profile is strongly related to the newest global trends in the development of physical chemistry and chemical physics. Scientific research is conducted in nine scientific departments. CHEMIPAN R&D Laboratories, operating as part of the Institute, implement, produce and commercialize specialist chemicals to be used, in particular, in agriculture and pharmaceutical industry. The Institute publishes approximately 200 original research papers annually.

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SCIENTIFIC PAPERS:

1. "Supramolecular organization of liquid-crystal dimers - bis-cyanobiphenyl alkanes on HOPG by scanning tunneling microscopy"
K. Krzyżewska, T. Jaroch, A. Maranda-Niedbała, D. Pociecha, E. Górecka, Z. Ahmed, Ch. Welch, G. H. Mehl, A. Proń, R. Nowakowski
Nanoscale, 2018, 10, 16201-16210
DOI: 10.1039/c8nr02069h

LINKS:

http://www.ichf.edu.pl/
The website of the Institute of Physical Chemistry of the Polish Academy of Sciences.

http://www.ichf.edu.pl/press/
Press releases of the Institute of Physical Chemistry of the Polish Academy of Sciences.

IMAGES:

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At the Institute of Physical Chemistry of the Polish Academy of Sciences in Warsaw, the first microscopic images were obtained depicting complex self-assembled structures in liquid crystal monolayers with molecular resolution. (Source: IPC PAS, Grzegorz Krzyzewski)

IChF181217b_fot02s.jpg **HR:** http://ichf.edu.pl/press/2018/12/IChF181217b_fot02.jpg
Microscope image of the CB8CB liquid crystal monolayer, made up of dimers with 6 carbon atoms. An example chiral windmill-like structure, formed of four dimers is marked, the seed of chirality in the crystal. (Source: IPC PAS)