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Our Institute

The Institute of Physical Chemistry of the PAS (IPC PAS), Warsaw, Poland, was established on 19 March 1955 as one of the first chemical institutes of the Polish Academy of Sciences.

In the recent assessment of the Polish Ministry of Science and Higher Education we were ranked third in Poland and first among the large chemical research organisations with more than 100 staff – we employ 175 scientists, including more than 50 professors. Every year our researchers publish nearly 200 original research papers in journals listed in the MSI Master Journal List, including periodicals with impact factor over 5 (“Science”, “Angewandte Chemie”, “Chemical Communications”, “Lab on Chip”, JACS, etc).

Our present scientific profile is strongly related to the global trends in the development of physical chemistry and chemical physics. Supported by state-of-the-art equipment, we conduct scientific research in nine scientific departments, dealing with physical chemistry of solids, surfaces, fluids and soft matter, quantum theory of solids and molecules, catalysis on metals, electrochemistry, corrosion, electrode processes, photochemistry, spectroscopy, complex systems and chemical information processing. In 30 project teams more than 80 research projects are currently underway. The Institute applies for about 30 patents a year, including international applications.

The CHEMIPAN Research and Development Laboratories, operating as a part of our Institute, implement, produce and commercialise specialist chemicals to be used in pharmaceutical industry, agriculture and forestry, including pheromones allowing for controlling pest populations.
As the first institute of the Polish Academy of Sciences, we took up shares in a spin-off company and became co-owner of Scope Fluidics, a spin-off company pursuing scientific research and designing microfluidic devices for medical and biotechnological applications.

We maintain collaborations with more than 40 universities and scientific institutions worldwide, we also take part in numerous national and international research projects. One of such undertakings is the over 73 million PLN project “Quantum semiconductor nanostructures for applications in biology and medicine”, aiming at construction of a semiconductor microsystem capable of fast and reliable detecting antibodies present in patient’s blood.

We have been awarded prestigious EU grants, including NOBLESSE (one of the largest grants awarded to a single Polish research institution under the activity “Research Potential” of the 7th EU Framework Programme) and microCODE (awarded under ERC Starting Grants).

The IPC PAS is authorised to confer academic degrees of doctor (doctorate) and doctor of science (habilitation) in chemical sciences, in the fields of physical and theoretical chemistry. The Institute runs a post-graduate International Doctoral Studies programme with currently more than 60 doctoral students. The Institute’s professors and doctors are involved in educational activities on the graduate and post-graduate levels.

We are initiators and co-organisers of the prestigious Golden Medal of Chemistry competition that is addressed to the authors of the best bachelor or bachelor of engineering theses in chemistry, including its borderlines with biology or physics in a given year.

In future, our activity will be focused around chemistry inspired by biology, chemistry related nanotechnology and the applications implemented using high tech companies.
ABOUT THE BOOK

We create knowledge to change the world
– this is the motto of our Institute. We take it seriously and regularly promote our scientific accomplishments, our researchers and our fields of science in Polish and international media.

Scientific accomplishments presented in this book are only a part of the research work performed at our Institute – the one that in recent two years attracted particular attention of Polish and international media due to press releases. In this short period of time, the reports on scientific successes of the IPC PAS have appeared at least several thousand times in internet services, fairly often reaching the main web pages of the largest Polish media and leading scientific and popular science web services, including so widely-read ones as ScienceDaily.com. The reports have been translated in over a dozen languages.

The presentation of research topics in this book is exclusively based on the press releases published by us. To enhance the legibility of the message, we divided the topics into four groups. The first group describes our basic research work. The second one is related to the detection techniques and methods that are of essential importance for chemistry. The third group is devoted to the research accomplishments with particular potential for application, and the last fourth group presents some of our activities related to organisational aspects of both our Institute and more generally of science.

To understand. To see. To make use. To organise.

That’s why we are for.
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SURPRISINGLY COMPLICATED MOLECULE IN OPEN SPACE

In interstellar clouds of extremely small density scientists managed to find a molecule that has an unexpectedly complicated structure. The discovery will force a change in the way of thinking about chemical processes occurring in the apparently empty areas of the Galaxy.

Translucent interstellar clouds are penetrated by highly energetic ultraviolet and cosmic radiation which can break any chemical species it meets. However, a group of scientists, the core of which is formed by Polish astrophysicists and astrochemists, managed to observe in such clouds a molecule made up of an unexpectedly large number of atoms: the diacetylene cation. Its discovery in the gas and dust clouds of small density may contribute to solving the oldest unsolved puzzle of spectroscopy. Studies were conducted mostly with the use of an 8-metre telescope in the Paranal Observatory in Chile by a group of scientists from the Nicolaus Copernicus University (NCU) in Toruń, Poland, the European Southern Observatory (ESO), the Seoul National University in Korea and from our Institute. The group is headed by Prof. Jacek Krełowski from the NCU’s Astronomical Centre.

The density of translucent interstellar clouds is extremely small. “The dilution of matter in such clouds corresponds to
the density obtained as a result of distributing one glass of air in an empty cube the face of which equals the area of a small country. This is much less than the best vacuum produced in a lab”, explains one of the co-finders, Assoc. Prof. Robert Kołos from the Laboratory Astrochemistry Group of our Institute. However, since interstellar clouds are of huge sizes, reaching dozens of light years, their gas molecules have a chance to interact with the penetrating radiation.

Spectroscopy is the field of science that deals with radiation-matter interactions. Molecules absorb and emit photons of specific energies only (and thus of specific wavelengths) corresponding to differences between energy levels typical for a given species. Consequently, as a result of interactions with diluted gases in translucent clouds, common in our and other galaxies, starlight that reaches the Earth is slightly changed. It lacks the waves of certain length – those absorbed by intervening interstellar atoms and molecules.

In the 1920s astrophysicists observed that light was absorbed by the interstellar medium in a manner that could not be explained by the presence of very simple components of interstellar gas known at that time. Today, with the use of radio waves, it is possible to detect quite big molecules – the record holder is cyanopolyne HC11N which comprises 13 atoms – but these are created inside dense, non-transparent clouds where they are protected from disruptive radiation.

“The peculiar optical properties of translucent clouds, connected with the presence of the so-called Diffuse Interstellar Bands DIB, have been a mystery for nearly 90 years. They are even called the longest standing unsolved problem of all spectroscopy”, says Prof. Krełowski (NCU), an authority in the field of optical spectroscopy of interstellar medium. The recent discovery allowed a new band to be added to the DIB set and, at the same time, to be identified as originating from the diacetylene cation H-CC-CC-H+.

“Diacetylene is a species unexpectedly big for translucent clouds. So far the compounds of no more than three atoms have been found there: carbon C3 and hydrogen H3+. In order to explain the presence of diacetylene cation we will have to revisit the existing astrochemical models”, adds Assoc. Prof. Kołos.

Asymmetric molecules – such as the cyanopolyne mentioned above, a linear sequence of carbon atoms with hydrogen at one end and nitrogen at the other – are able to emit or absorb the electromagnetic waves in the radiofrequency range. The high symmetry of diacetylene cation makes it invisible to radio telescopes, but present optical observations suggest this species to be quite a common component of the interstellar medium. It is detected not only in the two Galaxy regions that are especially rich in carbon, but also in averaged data coming from a dozen other lines of sight.

Following the detection of diacetylene cation it may be supposed that there are more diffuse interstellar bands generated by similar, symmetric molecules. “It seems probable that the DIB puzzle will soon be largely solved”, sums up Prof. Krełowski (NCU).
At a snail’s pace – this is how proteins should move inside living cells where viscosity of environment exceeds the viscosity of water even by million times. However, proteins move not much slower than in water! While looking for a solution to this puzzle, scientists from our Institute discovered a new principle of physics.

Why do biological processes occur in a nucleus? It is so overcrowded by macromolecules, so viscous, that proteins should move extremely slowly there. Under such conditions the pace at which proteins aggregate into complexes and at which molecules join DNA chains cannot be effective. “But we know that proteins in living cells move several hundred thousand faster than they should. We managed to discover why this is so”, says Prof. Robert Hołyst.

Human senses do not allow us to identify changes in viscosity well. The viscosity of rape oil seems to be relatively similar to the viscosity of water, though the latter is 400 times lower. Consequently, we often confuse viscosity and density. For example, shampoo comprises 95% of water and has similar density but due to its high viscosity it spills over a hand slowly. Honey is also viscous, not dense.

Viscosity appeared as a parameter in physics in the Navier-Stokes equations discovered in the 19th century. They describe river flow and air flow around plane wings correctly. According to this description, viscosity is not dependent on scale and should produce the same results in the case of a flying airplane and a protein particle moving inside a nucleus. However, measurements show something different. As early as in the 1950s, experiments, conducted in ultracentrifuges and concerning sedimentation of small particles at high load factors, revealed a surprising fact. It turned out that objects several billion times smaller can feel viscosity several thousand and even hundred thousand lower than a macroscopic object. A reason of such a dramatic change in viscosity could not be found for a long time.

Although viscosity was already examined by Newton, it has remained a mysterious property of nature to date. We understand its origin in gases: when two layers of gas move against each other, a molecule may jump from one layer to the other, there are collisions and the motion slows down. However, when gas becomes dense and turns into liquid, there are interactions between molecules and it is hard to indicate phenomena that are directly responsible for the origin of viscosity. As a result, scientists are still examining viscosity in the simplest real fluids made of atoms of argon and other noble gases.

A group of researchers from our Institute, under the direction of Prof. Holyst, has shown recently that in each hydrodynamic system there is a fundamental length scale at which there is a transition from macroviscosity to nanoviscosity. The size of this scale depends on the size of objects...
present in the fluid: in the case of polymers it will be the size of a random coil, and in the suspension of viruses – the length of a virus rod.

“If the size of a polymer coil is 10 nanometres, each object bigger than the coil, immersed in the polymer solution will feel macroscopic viscosity, and every smaller one – nanoviscosity”, explains Prof. Hołyst.

It is particularly interesting that changes in viscosity are exponential in length, which means that near the fundamental length scale they are very sharp. The decrease of the size of a floating object may result in the change of viscosity by as much as 5-6 orders of magnitude. The discovery of the researchers from our Institute means that the existing hydrodynamic equations – in which the parameter of viscosity is constant – will have to be reformulated in future.

The measurements were conducted as part of the research project with the use of the newest methods and equipment such as a confocal microscope with Fluorescence Correlation Spectroscopy. This new research technique allows the behaviour of individual protein molecules in liquids with capacity of cubical micrometers to be watched in the laser focus. The experiments were carried out for six years; for two years they were sponsored by the British concern Unilever, interested in the application of the results in the creation of new shampoos and conditioners.

From the scientific point of view, research on nanoviscosity is of fundamental importance, since nanoviscosity influences the rate of diffusion and limits the speed of biochemical reactions inside living cells. “It is not incidental that proteins in a cell, usually the small ones, create complexes only in the vicinity of a place where the biochemical reaction is to proceed. This is necessary since a large complex would move million times slower than each protein separately”, explains Prof. Hołyst.

Our scientists hope that their discovery will be used by industry, where viscosity plays a key role in many biochemical reactions. Producers of shampoos and cosmetics will certainly benefit from the results. The new principle of physics will also be important for the construction of nanodevices. “Science still hardly understands phenomena occurring at such a small scale. If we want to build nanomachines, we should learn as much as possible about phenomena typical for the world in which they are to work”, concludes Prof. Hołyst.

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Natalia Ziębacz, a PhD student, analyzes motion of nanoobjects using dynamic light scattering. (Source: IPC PAS/Grzegorz Krzyżewski)
Why a cloned cat looks different than the original? A new answer to that question is found by the researchers from our Institute. Using computer simulations and theoretical calculations they discovered a new statistical law. It explains the simplest and therefore probably the most widespread mechanism, by which a growing population of genetically identical cells forms groups performing different functions.

Under certain conditions, a population of reproducing cells can spontaneously divide into two groups with distinctly different functions. The researchers have since long been looking for the reasons of such a spectacular process but the mechanisms found so far were complicated and did not explain all observed cases.

It were only theoretical calculations and computer simulations carried out by scientists from our Institute that provided the simplest explanation. “We discovered a statistical law that is responsible for cell differentiation,” says Dr Anna Ochab-Marcinek. The new statistical mechanism will possibly allow to rationalize one of the sources of bacteria’s resistance to antibiotics and help understand, why monozygotic twins and cloned organisms are not their identical copies. A paper describing the discovery appeared in the “Proceedings of the National Academy of Sciences”, a prestigious scientific journal published by the US National Academy of Sciences.

Already in the middle of the past century it has been noticed in laboratory studies that an Escherichia coli population could divide into two groups with one of them showing expression of a specific gene, e.g., the gene responsible for production of an enzyme to
digest a specific type of sugar, whereas in the other group the same gene remained inactive. The effect is known in science as population bimodality.

The observation was intriguing, as all the cells had the same DNA and were kept under the same conditions. Moreover, despite the lack of changes in the gene set, subsequent cell generations were able to inherit new functions.

The researchers from our Institute set themselves the task of discovering the simplest possible mechanism that is responsible for such an unexpected behaviour of cells. For that purpose, they carried out theoretical calculations followed by a verification with a series of Monte Carlo simulations. The theoretical and computational work involved the most important chemical reactions that take place in a living cell.

The genetic information in cells is contained in the DNA structure, the proteins, however, are synthesised based on the sequences in the messenger RNA (mRNA). To produce a protein encoded in a gene, the information must be first transferred from DNA to mRNA. The transfer process (transcription) is controlled by molecules called transcription factors. After attachment to DNA, these molecules may repress (then they are called repressors) or promote (activators) the gene translation.

“A cell is a bag with a plenty of various molecules, moving randomly due to thermal motions. So, it may happen that after cell division one daughter cell will include more transcription factors than the other”, describes Dr Ochab-Marcinek. Using computer simulations, the researchers analysed, how a different number of repressors or activators affects the cell population.

The computer simulations carried out at our Institute mapped fluctuating concentrations of proteins produced by each cell during the development of population. As the number of molecules of a specific type in a cell is relatively low, the cell divisions result in an unequal distribution of repressors or activators among the daughter cells. As a result, the cell population growth leads to appearance of cells that produce a significantly more protein than other cells or do not produce it at all.

The dependence between the production rate of a specific protein and the number of repressors or activators in a cell is not proportional. The effect is referred to as a nonlinearity as the plot showing how the number of protein molecules depends on the number of transcription factors (the so-called transfer function) is not a straight line. The researchers from our Institute have shown that the nonlinearity is responsible for formation of two distinct groups in the population: in one of them the gene is active, whereas in the other – it is not.

The division of a cell population into two groups is of significant evolutionary importance. The differentiation increases the survival chance for a part of the population, if any changes unfavourably affecting one of the groups would occur in the environment.

“It is known that bacteria mutate and become more resistant to drugs. We have shown the simplest mechanism by which the very nature of bacteria and the underlying laws of statistics increase the survival probability of at least a part of the population, even if no mutations have occurred”, says Dr Ochab-Marcinek.

The researchers from our Institute have also introduced a simple method of geometric construction that can be used to predict when a specific cell population can develop a cell differentiation. The method consists in plotting of a straight line that intersects the axes of the coordinate system at points corresponding to the measured burst frequency of the transcription factor production in a population and the magnitude of these bursts. If the straight line intersects the gene response curve – known from the laboratory measurements – then the cell population starts to develop bimodality.

With such a simple geometrical operation one can easily explain the results of earlier experiments performed by other research groups, for instance the appearance of bimodality in population only at specific antibiotic concentrations.

“As the mechanism we discovered is the simplest among all possible ones, we suppose that, unavoidably, it is very common in cells”, says Dr Marcin Tabaka, a co-discoverer of the phenomenon. “The statistical law we discovered describes how a random disorder inside individual cells transforms into an order leading to a differentiation of population that is of benefit for its survival”, sums up Dr Ochab-Marcinek.

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POLYMERS IN BACTERIAL CYTOSKELETON

Existing beliefs as to the structure of polymers forming bacterial cytoskeleton have been partially erroneous, as proven by a team of researchers from our Institute. “We have shown that FtsZ polymers, elements of the bacterial cytoskeletons, are in fact very short, even a dozen times as short as believed so far”, says Dr. Sen Hou, the first author of a scientific publication that was published in the ‘Journal of Biological Chemistry’.

The cytoplasmic skeleton is a 3-dimensional network of protein fibres. Its share in the total cell mass is significant and usually accounts for over a dozen percent. In bacteria, the cytoskeleton plays a role similar to that of the spine in humans.

One of the most important cytoskeleton components are tubular structures that in eukaryotic cells (those containing nucleus) are made of a protein called tubulin and polymer fibres. It was believed even not long ago that the cytoplasmic skeleton occurs in eukaryotic cells only. The discoveries of the 1990s revealed, however, that it is also present in bacteria, where tubulin and its homologue, FtsZ protein, have been found.

FtsZ protein plays an important role in the process of bacterial cell division. That’s why such cytoskeleton of prokaryotes has been so intensely studied by the researchers looking for new antibiotics. Chemical compounds that would attack the cytoskeleton structure, would prevent the division of bacterial cells, and therefore efficiently inhibit the development of illness. The efficiency of such research heavily depends on the knowledge of structure of the polymers in the cytoplasmic skeleton.

The researchers at our Institute have studied the length of polymers formed by FtsZ proteins of Caulobacter crescentus bacteria. For the first time the dynamic light scattering (DLS) technique was used and proven to be highly usable in such measurements.

The DLS technique, also known as photon correlation spectroscopy, relies on recording light scattered due to motions of molecules, e.g., Brownian motions. The scattering is the more uniform the smaller are the molecules present in the solution. The DLS allows to measure molecular sizes below one micrometer and to study processes with duration from microseconds to minutes.

The dynamic light scattering measurements performed by the team from the IPC PAS led to an unexpected observation. It has been found that a typical fibre of FtsZ protein is in fact very short. It is composed of 9–18 monomers only, and its total length is ca. 100 nanometers, i.e., dozens of times less than assumed so far based on measurements carried out with transmission electron microscopy (TEM).

By increasing and decreasing the polymerisation rate of samples, the researchers from the IPC PAS have shown that when FtsZ solution contacts a copper grid surface used in sample preparation for transmission electron microscopy, small linear polymers start to form large bundles within a few seconds. So, the overestimated lengths of cytoskeletal polymers accepted in the world literature resulted from the procedure of sample preparation for transmission electron microscopy.

“Our result is not only well documented, but it also better fits to the present knowledge of chemical environment in the cell interior. The nanoviscosity of the cytoplasm in bacteria is up to a dozen thousand times as high as that of water. Had the cytoskeleton polymers been long, they would not have been able to move so fast in the cytoplasm”, says Prof. Robert Hołyst.

The work on the polymers of FtsZ protein has been financed from an interdisciplinary research grant awarded by the Human Frontier Science Program Organization and by the European Union from the European Funds for Regional Development under a TEAM grant from the Foundation for Polish Science.
Physicists agree that laminar flow of liquids has been well understood and described in detail from the theoretical point of view. Our researchers, however, discovered a new phenomenon related to the fluid dynamics. It occurs when minute droplets translate through microfluidic channels.

“The effect observed by our group is related to changes in swirls inside microdroplets and as yet has not been predicted by existing theoretical models”, says Dr Sławomir Jakieła. The results of the research, pursued thanks to a TEAM grant from the Foundation for Polish Science, were published in a prestigious physical journal “Physical Review Letters”.

Microfluidic systems are miniature chemical reactors of a credit card in size, or even less. Inside these systems, microchannels with diameters of tenths or hundredths of a millimeter provide a path for laminar flow of a carrier fluid (commonly oil) with floating microdroplets of appropriate chemical compounds.

“Using a single microfluidic system, even today one can carry out as much as a few tens of thousands of different chemical reactions a day. In future, these systems will become for chemistry what integrated circuits turned out to be for electronics. Yet before we build chemical devices as revolutionary as silicon microprocessors, we have to reach a comprehensive understanding of all physical phenomena occurring in flows of microdroplets”, continues Dr Jakieła.

The flows that we experience at the macroscale are often dominated by inertia and turbulences. With small volumes that are typical for microfluidic systems, the flow of a liquid is laminar and subject to viscosity-related effects.

Microfluidic systems are miniature chemical reactors of a credit card in size, or even less. Inside these systems, microchannels with diameters of tenths or hundredths of a millimeter provide a path for laminar flow of a carrier fluid (commonly oil) with floating microdroplets of appropriate chemical compounds.

The speed of oil flowing in microchannels is not uniform. The layers close to the walls move with the lowest speed, whereas those near the middle of a channel – with the highest speed. “If a microdroplet is distinctly smaller than the channel diameter, it can find a place in the middle part of the flow, reaching the speed even twice as high as the average oil speed. This is nothing surprising. Similar effect can be observed for instance in rivers: the current near the banks is much slower than in the middle of the river”, explains Sylwia Makulska, a PhD student.

If a sufficiently large droplet flows in a circular channel, it occupies almost the entire lumen of the channel. The droplet speed is then almost identical as that of the oil flow. The situation gets much more interesting when the droplet translates in rectangular channels that are typical to microfluidic systems. Due to interfacial tension, the cross-section of a microdroplet remains rounded leaving the corners of the channel free for the flow of oil.

The team from our Institute produced microdroplets from aqueous solutions of glycerine of different concentrations, and therefore of different viscosities. They translated in oil (hexadecane) through a 10 cm long rectangular channel. The researchers measured the speed of microdroplets relative to the oil as a function of their volume (length in a microchannel), droplet and oil viscosities and the flow speed of the carrier liquid.

When the viscosity of microdroplets was less than or comparable to that of the carrier liquid, their speed relative to the oil turned out to decrease with increasing droplet length, but in a certain range only. The droplets were translating with the lowest speed when their length was two, three times greater than the channel width. “Every time we observed the
translate under some conditions faster and under other conditions slower relative to oil”, concludes Jakieła.

To find out what is the reason for the surprising behaviour of the droplets, our researchers introduced to microdroplets fluorescent markers of a few micrometers in size. When the droplets were moving along the microchannel, they were irradiated with laser light to excite fluorescence of the markers, which allowed for observation of fluid movements inside the droplets.

The measurements revealed that the distribution of swirls inside a droplet changes with increasing flow rate of the carrier liquid. “We expected changes, but the existing theories suggested that the number of swirls in microdroplets decreases with increasing oil flow rate. We observed, meanwhile, an opposite phenomenon: the faster was the oil flow, the more swirls were in a droplet. The Nature played again a trick on theoreticians”, sums up Assoc. Prof. Piotr Garstecki.

The work has started to make use of the new phenomenon in processes related to mixing the contents of microdroplets in microfluidic systems.

minimum speed relative to oil. Everything seemed to be in line with what the theoreticians would expect”, says Jakieła.

But what was really interesting were things that happened when the researchers started to change the rate of oil flow. It turned out that the minimum of the droplet speed relative to oil was disappearing with increasing flow rate. Further increase in the oil flow rate resulted, however, in reappearance of the minimum – but this time deeper and wider.

“To make the long story short: we discovered that, depending on the oil flow rate, a droplet of specific length can

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MOLECULAR HEDGEHOG MAY ASSIST DRUG DELIVERY

Like a rolled-up hedgehog – so looks an aggregate composed of twelve calixarene molecules, obtained and examined by our researchers. They managed to crystallise the self-assembled inverted micelle-like structure which allowed them to get a deeper insight into its molecular structure at the atomic level. The aggregate has a spacious cavity in its central part that can be used to transport other molecules, e.g., drugs.

Calixarenes are organic compounds with cyclic molecules composed of phenyl units. The simplest representative of the family is calix[4]arene, consisting of four phenyl units with a cavity in the centre. The cavity is sufficiently large to host another molecule, entirely or in part, to form a molecular complex.

“In practice, we consider calixarenes as molecular analogues of chalices or baskets that can be used to transport...
other molecules, for instance drugs. Our group, together with colleges from the Institut de Biologie et Chimie des Protéines in Lyon, has an international patent for producing co-crystals of calixarenes with drugs”, says Prof. Kinga Suwińska. 

To use calixarenes in medicine is not easy. These compounds are usually soluble only in organic solvents. Therefore, the researchers at the IPC PAS study modified calixarenes, substituted with sulphonate (–SO3H) or phosphonate (–PO3H2) groups. This way, calixarenes are converted into acidic form and become water-soluble.

Tests on mice, performed two years ago by a research team from the Institut de Biologie et Chimie des Protéines, collaborating with our Institute, showed that sulphonated calixarenes are not toxic in low and medium concentrations. In addition, sulphonated calixarenes show themselves biological activity, e.g., they have antiviral and antibacterial properties.

Modified calixarenes are potential drug carriers. Their importance is the higher, as the drugs, which in pure form are water-insoluble, can become water-soluble in a complex with appropriate calixarene. Furthermore, complex formation may enhance the drug’s bioavailability profile. This means that drugs – after all not always immaterial to patients’ tissues and organs – can in future be administered in lower, safer doses.

Designing appropriate complex with calixarene, researchers are able to protect complexed molecules against external factors like light or moisture. It has important practical significance. In pure form, a drug may decompose, e.g., in the upper part of the digestive tract. With calixarenes, the drug can be protected like in molecular capsule and in this form can be delivered precisely where its presence will be most desirable.

The most recent discovery of the IPC PAS’s supramolecular chemistry research group are modified calixarene molecules self-assembling into aggregates with exceptionally complex and visually appealing structure. The story began with obtaining a new calixarene derivative that crystallised as regular crystals.

“Crystalline compounds are excellent research objects. Their structure can be directly analysed using X-ray diffraction. That’s why we were able to determine so precisely, how the new calixarene molecules self-assemble”, explains Prof. Suwińska.

It turns out that under certain conditions, twelve calixarene molecules assemble forming spherical structure with alcylo carbonyl groups pointing outwards. The emerging supramolecular supermolecule resembles a rolled-up hedgehog.

The picturesque supermolecule discovered in our Institute is about five nanometers (billionth parts of meter) in size. Particularly important for the potential future applications is a presence of large internal void with a volume of about thousand cubic angstroms.

“In the scale of the microworld such a space is really something. Inside you can put more than 30 water molecules”, says Prof. Suwińska. Due to its special structure, molecular hedgehog from our Institute seems to be an ideal candidate for transporting other molecules.

Prof. Suwińska makes clear that the studies conducted in the Institute of Physical Chemistry of the PAS have so far an exploratory character. Development of methods for producing such and analogous calixarene supermolecules, examination of properties of their complexes with other molecules including drugs, and testing such complexes for their possible toxicity and/or biological activity, will require long studies in collaboration with other research groups. ■

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EVERYTHING EVAPORATES. NO ONE KNOWS: HOW?

Evaporation takes place all the time in our environment. The phenomenon plays an important role in the formation of the Earth’s ecosystem and life of many organisms, in particular humans, who use it to stabilise their body temperature. “The first scientific publication concerning the mechanism of evaporation was written by a famous physicist James Clerk Maxwell. We showed that it contained an error that has been repeated for the last 130 years”, says Prof. Robert Holyst. The computer simulations allowed some of the puzzles, connected with the evaporation of a liquid into vacuum or its own vapour, to be solved. In cooperation with the Institute of Physics of the PAS, our scientists are preparing a series of experiments that will allow them to verify the correctness of the model in the case of the evaporation of drops of water into air.

Although evaporation is so common and it plays a big role in the environment, little attention has been given to the phenomenon. “Our studies also originated accidentally, as it often happens in science”, says Prof. Holyst. “Several years ago, in our Institute it was necessary to test a new program for calculations relating to fluid dynamics. We decided to check the simulator using a popular problem. We chose evaporation because we thought that since the phenomenon was so common and the subject was known for over one hundred years, everybody knew well what happened during the process. However, after we had made calculations using the existing formulas, it turned out that many things simply did not add up”.

Our scientists developed their own theoretical model of the phenomenon and then carried out computer simulations illustrating the process of evaporation of nanodrops into their own vapour or vacuum. The starting point was a drop of liquid closed in a vessel, and in equilibrium with its vapour. In some computer simulations the walls were heated, in some others the vapour was removed, and in the others not only was the vapour removed but the temperature of the system was maintained constant.

During evaporation the most interesting events take place on the border of a liquid and a vapour. The thickness of this interface is more or less equal to the diameter of an atom. The simulation of evaporation in a relatively small cube with faces one meter long would require the calculation of dozens of milliards of points along each of the three dimensional axes. The total number of points would increase to billion of trillions, which exceeds calculation abilities of modern and future computers. In order to deal with this obstacle, our scientists analysed the system of a size of only 1 cm, in which a drop of a diameter of approx. 70 micrometers evaporated. In addition, thanks to the use of symmetry, it was possible to reduce the theoretical description from three-dimensional to one-dimensional. The results of simulation agreed perfectly with the available measurement data.

“Maxwell assumed that evaporation took place at constant temperature. It is so, if we look at the initial state, that is a liquid, and the final state, that is a vapour. It is true that their temperatures are equal. But during the evaporation process itself, the nature acts in a completely different way”, explains Assoc. Prof. Marek Litniewski.

The existing description assumed that the heat transfer in the system was stable and the rate of evaporation was limited by the efficiency of the process during which the particles break away from the surface of drops, i.e. diffusion. However, the simulation showed that during the evaporation into vacuum or the liquid’s own vapour the system gained mechanical equilibrium very quickly. Particles break away from the surface of a liquid and their mechanical recoil allows the equalisation of the pressure inside the drop. If the rate of evaporation on the surface achieved the maximum value and the system was still unable to equalise the pressures, spaces with new surfaces would open inside the drop and it would start to boil. However, it was observed that the mechanical equilibration of pressure can be insufficient and the temperature on the surface of the liquid decreases: the drop aims at maintaining the pressure equilibrium at the cost of its internal energy. This observation suggests that the factor that is crucial during evaporation is not the diffusion of particles into the environment but the heat transfer and the equality of pressures.

The experimental part will be carried out by scientists from the Institute of Physics of the PAS, headed by Assoc. Prof. Krystyna Kolwas. Physicists from the IP PAS have already observed the evaporation of microdrops of a liquid into the liquid’s own vapour or vacuum. Drops of micrometric sizes were used in the experiments. Since their surface was electrically charged, the drops could be caught by the electric field, lighted by a laser and, while recording changes in interference patterns, it could be observed how their size changed during the evaporation. Currently, thanks to a new measurement chamber with precisely controlled pressure and chemical composition of the atmosphere, a series of experiments...
on evaporation into air can be conducted, and consequently, it will be possible to determine which factor has a decisive influence on evaporation in the situation where pressures are equalised from the beginning. The results of the experiments along with computer simulations will allow creating a comprehensive picture of the process of evaporation of water drops in the conditions maximally similar to those that exist in nature.

The deeper understanding of physical mechanisms responsible for evaporation will affect many areas of human activity. Better climate models will allow more precise forecast of weather changes in a short and long time perspective, and more efficient devices for cooling processors and lasers will be developed. Since in engines the evaporation of fuel micro-drops injected into a combustion chamber must precede the ignition, the knowledge of evaporation will allow increasing car efficiency in future. “Our research shows that old formulas are still worth being examined”, sums up Prof. Hołyst.

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VISCOSITY OF THE CYTOPLASM IN CANCER CELLS

Small protein molecules almost do not experience the cytoplasm viscosity while moving within the cell. Our researchers have described in a physically consistent manner the changes in viscosity as measured in various solutions and experienced by probes with size varying from a nano to a macro scale. Their findings were published by the prestigious “Nano Letters” journal.

“We improved our earlier formulae and conclusions to successfully apply them to a larger number of systems, including the first description of the cytoplasm viscosity in cancer cells”, says Prof. Robert Holyst.

The very first scientific publication to address the viscosity of complex fluids was a paper by Albert Einstein from 1906. In the time that followed intriguing evidence has been presented with regard to the cytoplasm viscosity in cells. This experimental evidence indicated that in spite of a high cytoplasm viscosity the mobility of small proteins in the cytoplasm is high – many orders of magnitude higher than the Stokes-Sutherland-Einstein formula would imply.

The researchers from our Institute managed to describe the viscosity changes using one phenomenological formula containing coefficients of the same physical nature. The coefficients give a description for both the fluid medium (filled, for instance, with a network of long-chained polymers or clusters of molecules) and the probe (e.g., protein molecule) moving in the medium.

The new formula is of universal importance and can be used for probes from a fraction of nanometer up to centimeters in size. The relationships found are generally valid for various types of fluids including solutions with elastic microscopic structure (e.g., polymer networks in various solvents) and microscopically rigid systems (e.g., composed of elongated aggregates of molecules – micelles).

In the “Nano Letters” report our researchers applied the new formula to describe the mobility of DNA fragments and other probes in mouse muscle cells (Swiss 3T3) and human cancer cells (HeLa). “We managed to show that the fluid viscosity in the cell depends actually not only on the intracellular structure but also on the size of the probe used in viscosity measurement”, says Dr Tomasz Kalwarczyk.

The viscosity does not depend only on the microscopic structure of a complex fluid (in the picture a cable coil represents polymer coils in a liquid), but also on the size of the probe used (represented by a tennis ball in the demonstration). The phenomenon is presented by Dr Tomasz Kalwarczyk. (Source: IPC PAS/Grzegorz Krzyżewski)
The researchers from our Institute measured the so-called correlation length that in the cytoplasm of the Swiss 3T3 cells was 7 nanometers (a billionth part of a meter), and in the HeLa cells – 5 nm. The correlation length is a limiting parameter for viscosity – the proteins smaller in size than the correlation length move freely in the cell.

Another limiting parameter determined in the study was the hydrodynamic radius of the objects the fluid is made of. This is also an essential parameter, as the probes larger than the hydrodynamic radius experience macroscopic viscosity (the probes larger than the correlation length but smaller than the hydrodynamic radius experience viscosity that increases dramatically with probe size). It turned out that in the HeLa cells, the macroscopic viscosity was experienced by probes larger than 350 nm, whereas in the Swiss 3T3 cells the threshold was 120 nm only.

“Our research resulted in a novel method to characterise cell structure – by measuring the viscosity of the cytoplasm”, stresses Dr Kalwarczyk.

The outcome of the research presented by the scientists from our Institute will allow to estimate better the migration time of drugs introduced in cells, and will be also applied in nanotechnologies, for instance in fabrication of nanoparticles with micellar solutions.

The findings of the study are also of significant importance for advanced measurement methods, such as dynamic light scattering, that allow to analyse suspensions of molecules by their sizes. If the dependence of viscosity on the size of the viscosity probe used is not taken into account, the results of the measurements can be affected by significant errors.

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MORE CAN BE DONE FASTER AND EASIER THAN LESS

Nothing is self-evident in the world of quantum phenomena. Already a couple of years ago a surprising fact has been discovered in our Institute: two hydrogen atoms in the central part of porphycene molecule move easier and faster together than each of them individually. Only recently, however, the researchers succeeded in finding the answer why it happens. The outcome of the study is not only of scientific importance but can also be used in advanced medical therapies, including cancer treatments.

Derivatives of porphyrin, a substance present, i.a., in human blood, have been studied at our Institute for about a dozen years. One of them is porphycene $\text{C}_{20}\text{H}_{14}\text{N}_4$.

Porphycene molecules have a form of a flat carbon ring with hydrogen atoms outside and four nitrogen atoms inside the ring. The empty space in the centre of the molecule contains two hydrogen atoms, permanently tunnelling between nitrogens.

The measurements using experimental techniques developed at the IPC PAS allowed to spot these ultrafast processes. To the researchers’ surprise it turned out that both internal hydrogen atoms tunnel easier and faster when they do it concertedly. Another series of experiments, completed recently, allowed us to develop a theoretical model explaining the essence of the surprising phenomenon. And by the...
The tunnelling mechanism explains why quantum objects are able to overcome potential barriers without the need to acquire energy. “Imagine we are standing in front of a wall. To get through we need first to accumulate energy that is needed to climb the wall. A quantum particle is able, however, just to disappear on one side of the wall and to reappear on the other”, describes Dr Piotr Fita from the Faculty of Physics of the Warsaw University.

“Already the question alone of whether whole hydrogen atoms or only protons do tunnel in porphycene, excited a lot of emotions among scientists”, says Prof. Waluk. A hydrogen atom consists of a proton and an electron around the proton. When hydrogen becomes a part of a molecule, the electron joins molecular electron cloud (thus playing a role of an adhesive keeping the nuclei together). A tunnelling of proton would indicate that electron density in the electron cloud after the process is completed would remain unchanged. If the entire hydrogen atom had tunneled, then the electron would have followed the proton. “The real life is usually neither this nor that”, explains Prof. Waluk. “When the proton tunnels in the molecule, only a part of electron density in the cloud is following it”.

A porphycene molecule can oscillate in 108 vibrational modes. The scientists from our Institute have shown already earlier that proton tunnelling can proceed faster or slower, depending on the vibrational state of the molecule. Recent experimental studies and theoretical models have shown that when one proton is transferred, the energy of the molecule changes and it must appropriately modify its structure, whereas when two protons tunnel simultaneously, the energy remains unchanged. The atoms in the molecule do not need to be reorganised then and the tunnelling becomes easier.

Initially, tunnelling was considered to be a rare phenomenon to occur only under sophisticated conditions. It becomes obvious today for an increasingly large number of chemists that tunnelling is a common process occurring in most – if not in all – chemical reactions. Also the biologists change their approach along similar lines. It is assumed that tunnelling plays a significant role in hydrogen transfer in enzymes. It seems that a synchronous, simultaneous tunnelling of several protons is not a rare phenomenon, helping to avoid reorganisation of a massive skeleton of the molecule. Similar mechanism may be important in formation of DNA mutations.

In recent experiments, carried out at the Faculty of Physics of the Warsaw University and our Institute, porphycene was studied in solutions. The tunnelling was monitored with laser techniques allowing for measurements with time resolution down to 50 femtosecond (1 fs = 10^-15 s, i.e., one quadrillionth part of a second). It has been shown that the way the tunnelling hydrogen behaves has a significant effect on the lifetime of fluorescence, i.e. light emission by the molecule. At room temperature in highly viscous solutions, the fluorescence lifetime increased even by thousand times: from picoseconds (1 ps = 10^-12 s) to nanoseconds (1 ns = 10^-9 s).

The excited porphycene molecule could be used as a probe for viscosity measurements in micro- and nanoscale. When used appropriately, it would allow to observe selected parts of cells and to detect their certain pathologic conditions. Because of strong dependence of oxidative properties on solution viscosity, porphycene derivatives described by our researchers open also interesting prospects for selective killing of cancer cells with photodynamic therapies.

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GIVE SUPPORT TO REPULSION, AND YOU’LL SEE AtTRACTION

When two objects repel each other under the action of one force, we usually expect that addition of another force, also repulsive one, will accelerate separation. This intuitive view is, however, not always true. Researchers at our Institute have managed to explain surprising results of experiments with mixtures, where two repulsive interactions have lead to a strong attraction.

The results of last year’s experiments with mixtures carried out at the University of Stuttgart, Germany, were really surprising. In one of the systems studied, a repulsive force was acting between the system components. When a second repulsive force was introduced, an unexpected effect was observed: a strong attraction. This unusual result aroused interest of the theoreticians from our Institute.

“Starting from the basics, we have developed a theoretical model of the system studied in Germany and successfully verified its predictions with experimental evidence. That’s why we are able to explain, how superposition of two repulsive interactions transforms into attraction”, says Prof. Alina Ciach.

The research has been completed under the International PhD Projects Programme of the Foundation for Polish Science and co-funded from the Innovative Economy Operational Programme of the European Union.

The system modelled was a mixture of water and an oily organic liquid – lutidine. The mixture included also salt ions. The fluid was placed between two electrically charged walls, one hydrophilic, and another one hydrophobic.

Water is miscible with lutidine only in a certain temperature range. An interesting situation arises close to the critical temperature, where the system cannot “make a decision” if the components should mix or separate.

“Under these conditions, the water layer at the hydrophilic wall becomes relatively thick, similarly as the oil layer at the hydrophobic wall. And as water and oil ‘dislike’ each other, a force emerges to push the walls apart”, explains Faezeh Pousaneh from Iran, a PhD student working at the IPC PAS under the International PhD Projects Programme of the Foundation for Polish Science.

The unusual behaviour of the modelled system was revealed after electric charge of the same sign was applied to both walls. A second, electrostatic, repulsion was acting then between the walls, and even so the walls were becoming attractive! “Paper and pencils were set in motion. Using purely analytical calculations, together with Faezeh, we derived specific formulae to describe the course of the phenomenon”, says Prof. Ciach.

It turned out that the key element of the model was the assumption that the ions in solution move exclusively in water, while avoiding lutidine. The walls of the system under study were electrically charged, so they attracted ions. “But there is lutidine layer at the hydrophobic wall!”, notices Pousaneh. “So an ion faces a dilemma: it wants to get to the wall, but the access is protected by lutidine. And the hurdle can be taken in one way only: by pulling water”. As a result of the process described above, the wall surface, earlier hydrophobic, starts to behave like a hydrophilic one, becoming similar in that respect to the other wall. And two hydrophilic walls attract each other.

The team from our Institute intends to continue the research on variants of the modelled systems. “Interactions similar to those described by us occur between charged colloidal particles with selective surfaces. Depending on temperature, the interactions are sometimes repulsive, sometimes attractive”, says Prof. Ciach. It turns out that in a narrow temperature range, the potential has a minimum for certain distance between the particles, so it is similar to that one being responsible for arrangement of atoms in nodes of the crystal lattice. “Thus, by controlling temperature we will be able to force a colloid to develop a specific structure. Then it can be preserved and used, for instance in material engineering”, stresses Prof. Ciach.

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Faezeh Pousaneh, a PhD student, with a “kitchen-like” version of the mixture under study. The fruits symbolize colloid particles, white grains – water, dark – lutidine, red – water-prefering ions. (Source: IPC PAS, Grzegorz Krzyżewski)
Organic materials will change the face of electronics. Devices will become not only cheaper, thinner and lighter but will also gain unprecedented properties. It will be possible to roll a display into a tube or produce it from transparent elements and place directly on windows, for instance, in cars. However, before elastic electronics wins the mass market, the rules governing the fabrication of ordered thin layers of organic semiconductors must be learnt. A group of scientists from our Institute (headed by Assoc. Prof. Robert Nowakowski), the Warsaw University of Technology (Prof. Małgorzata Zagórska) and the Atomic Energy Commission in Grenoble (Prof. Adam Proń) has achieved considerable progress in this respect.

“We have examined how the organisation of molecules changes within layers, depending on the length of molecules. Thanks to this we understand why shorter molecules form ordered two-dimensional structures, while their long analogues create chaotic aggregates. We can sometimes eliminate this last effect completely”, says Prof. Robert Nowakowski (IPC PAS).

Organic molecules may conduct current as well as metals. However, in metals electron cloud can move in any direction whereas current carriers in organic molecules move along the so-called conjugated double bonds. This means that carriers are very mobile only in one direction: along the long axis of the molecule. In this situation the conductivity can be improved in layers consisting of very long molecules, that is by using high-molecular compounds – polymers. However, this solution has a significant drawback. It is more difficult for high-molecular compounds (polymers) to create ordered layers. As a result they often arrange themselves randomly, which leads to the chaotic movement of charge carriers (the carrier, having passed through a long macro-molecule of coil-like shape, may reappear nearly in the same place in which it started its journey). The chaotic structure leads to low charge carriers mobility. The problem described
above can be solved through the use of molecules that are longer than typical organic molecules but in the same time short enough to show natural tendency to self-ordering, i.e. oligomers. As a result of mutual interactions such molecules arrange themselves into parallel rows.

At present it is assumed that in future, organic electronic systems will be made from ordered layers of molecules that guarantee high mobility of carriers in the direction specified for a given device. The optimisation of structure of organic semiconductor layers consists in finding a compromise between the length of an oligomer chain and its self-organisation ability. “Chemists from the Warsaw University of Technology prepared for us new polymers and oligomers, derivatives of thiophene. However, the structural and microscopic examination of thin layers of these compounds showed that they were disordered. We suspected that this disorder resulted from polydispersity, that is the coexistence of molecules of different lengths. This phenomenon occurs in almost all synthetic polymers”, explains Prof. Nowakowski. In order to verify this assumption, our scientists developed a unique method for the separation of a mixture after polymerisation into fractions of molecules of identical length. High performance liquid chromatography and thin layer chromatography were used for this purpose. Then monolayers were deposited on a graphite substrate from these fractions, and they were examined with the use of a scanning tunnelling microscope.

The ordering of molecules is connected with the existence of long and elastic alkyl groups introduced into a molecule to increase its solubility. The shortest molecules create two-dimensional structures in the layer as a result of mutual interaction (interdigitation) of alkyl groups of neighbouring molecules in two perpendicular directions. The elongation of a molecule increases the number of alkyl groups interacting only perpendicularly to its longitudinal axis and leads to the asymmetry of intermolecular interactions. This results in the change of the type of ordering from two-dimensional islands, observed for shorter oligomers, into one-dimensional columns created by longer oligomers. “Chaos in the layers is caused by the fact that they are created from a mixture of macromolecules of various lengths, each of which aims at a different type of ordering”, says our PhD student Tomasz Jaroch.

The ordering of molecules in a layer has its origin in their structure. Even a small change in the structure of a mer (a repeat unit from which a polymer or oligomer chain is made) may affect the self-organisation process. The group of Prof. Zagórska (WUT) synthesised oligomers with alkyl groups attached to the carbon atoms of the thiophene ring in different positions as compared to the case of oligomers examined previously.

This change results in a decrease of the distance between alkyl groups within the mer unit and consequently, a change in interactions between molecules in the layer. In compounds synthesised in this way no negative effects of self-organisation have been observed: molecules of different lengths created ordered two-dimensional islands. The ordered layers prepared in this way show good semiconducting properties because the cores interacting directly along the oblong axis guarantee an increase in the effective mobility of charge carriers. Our researchers confirmed experimentally the lack of interdigitation of the alkyl groups in this direction by demonstrating on microscopic pictures that it was possible to move a single oligomer within the layer. The interdigitation of alkyl groups along the axis of a molecule would make such an operation impossible.

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MOLECULAR “PROPELLERS” MAY ROTATE VERY SLOWLY

In the liquid-crystal layers that are several nanometers thick and created on water surface, molecules may rotate with extremely low speed, just one revolution per several minutes. Such slow rotational motion is a real surprise since it was expected that rotation would be quickly destroyed by thermal fluctuations.

“The slowdown in rotation of molecules is nothing unexpected in liquid crystals usually formed of thousands of layers. However, in our experiments we have monolayers and we can observe the effects of very slow rotational motion of chemical molecules nearly with the naked eye”, emphasises Dr Andrzej Żywociński.

The experiment conducted in our Institute is distantly related to famous experiments carried out by Benjamin Franklin and connected with quieting agitated water by spilling oil on it. During one of the attempts Franklin noticed that oil spilled on the surface of a pond became so thin at a certain point that it stopped spreading. “We do something similar but on a smaller scale: we spill microlitres of liquid crystal on water surface. Its molecules form a monolayer, that is a layer which is one-molecule thick”, explains Dr Żywociński.

Molecules of the liquid crystals that are examined have amphiphilic character – the hydrophilic group of a chain attaches to water surface, over which the hydrophobic tail protrudes making dissolution impossible – and they freely move across the water surface, which means they behave like gas in two-dimensional space. However, researchers were interested in the behaviour of liquid crystals in a liquid phase.

A gas may be transformed into a liquid or solid as a result of changes in temperature or pressure. If we use the latter, solidification is achieved at high pressures of at least several dozens of atmospheres. Fortunately, in the case of monolayers a suitably high pressure can be easily obtained with a device called the Langmuir balance. It is a shallow tank filled with water, with two hydrophilic barriers between which there is a film of the liquid crystal several nanometers thick.

“It is sufficient to decrease the distance between the barriers in order to achieve an increase in surface

Dr Andrzej Żywociński and a PhD student Patrycja Nitoń near the Langmuir tank with the use of which they examine liquid-crystal monolayers on the water surface. (Source: IPC PAS, Grzegorz Krzyżewski)
pressure that will cause the liquid crystal to become liquid or even solid*, says Patrycja Nitoń, a PhD student.

The surface of a liquid-crystal film in a liquid phase was observed with the Brewster angle microscope at relatively small enlargement. The Brewster angle is an angle at which light falling on the surface of a dielectric reflects off fully linearly polarized, which means that the component of the electric field oscillates in one plane. If a polarizer is placed in the way of such polarized light so that the light goes through it, it will stop the entire reflected light and under the Brewster angle microscope clean water will look black. However, if on the water surface there is something which twists the plane of polarization, bright reflections will appear.

In the experiments conducted in our Institute it was analysed how a monolayer of a ferroelectric SmC* liquid crystal behaved on water surface. It is typical for SmC* phase that molecules spontaneously arrange themselves into layers and each subsequent layer is slightly twisted in relation to the others. "We have only one layer which we can imagine to be a forest of molecules inclined in the same direction at certain angle*, explains Dr Żywociński. When water molecules evaporate, they hit into groups of atoms of various sizes which are connected with an asymmetric (chiral) carbon atom in each molecule of the liquid crystal. Due to the asymmetry, the fragments of molecules of liquid crystals protruding over the water surface act as the sails of a windmill and they start to rotate collectively (this effect was for the first time observed by Prof. Hiroshi Yokoyama from Japan).

A molecule must be constructed in an appropriate way to be able to rotate. The polar group that keeps it at the water surface should not be too big as it would be immersed too deeply and would hinder the rotation caused by the asymmetric chiral group which is hit by the molecules of evaporating water. The chiral group, on the other hand, must remain distinctly above the surface.

Rotating molecules change the polarization plane of the reflected light and in the field of view of the Brewster angle microscope there are areas of periodically changing brightness. The quickest rotation of molecules observed in this way lasted five seconds and the slowest as long as eight minutes. It is probably possible to achieve even slower rotational motion but not through the decrease of temperature (as liquid crystals become solid then) but by saturating the air with water vapour, which would decrease the pace of evaporation and thus the frequency of collision of water molecules and "sails" of liquid crystals.

Slowly rotating molecules of liquid crystals can be used to construct nanodevices. “It is possible to construct a molecule in which a group of atoms playing the role of a sail would be a kind of a nanodrive. Then we would create a real molecular nanoengine driven by a water vapour stream", says Dr Żyzwociński, and he adds that scientists are now working on the possibility to transfer this collective rotation of single molecules to larger objects.

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ROLE OF NOISE IN SPINE FORMATION

In an early stage of embryogenesis in vertebrates, periodic segments called somites are formed in their dorsal mesoderm. With time, they transform into, i.a., vertebrae, spine elements. The development of these periodic structures in embryos is controlled not by genes, but by simple physical and chemical phenomena. A Polish-French team from the Centre National de la Recherche Scientifique, University Pierre et Marie Curie and our Institute have proposed a straightforward theoretical model to describe the process. An analysis of the model properties has revealed that the formation of periodic patterns is surprisingly affected by the internal noise that is present in any physical system.

“We are convinced that the laws of physics and chemistry can explain biological phenomena and the evolution of living organisms”, says Assoc. Prof. Bogdan Nowakowski. “That’s why we attempted to model theoretically one of the elements of vertebrate embryogenesis: the formation of periodic structures in somitogenesis. We did it by considering the minimal scheme of chemical reactions involving only a few components”.

The chemistry of far-from-equilibrium phenomena knows spectacular Belousov-Zhabotinsky oscillating reactions (you can watch them in many movies on Youtube). The reactions occur in aqueous solutions of appropriate reagents with various concentrations. If addition of a component results in deviation of the system from the state of thermodynamic equilibrium, then chemical wavefronts start to propagate in the liquid. Their existence results in periodic colour changes of the solution. If the reaction takes place in a thin solution layer, e.g., in a Petri dish, one can observe permanently forming and propagating colour rings.

The model proposed by the scientists from CNRS, UPMC and our Institute is exceptionally straightforward. It involves three chemical reactions and four substances including two ones forcing a non-equilibrium state in the system under study. The parameters of the model are adjusted so as to induce reactions leading to clear spatial oscillations of concentrations of the solution components. The result are periodic patterns, stable in time, so called Turing structures.

In nature, periodic structures in embryos are probably formed in a more complicated way, involving perhaps several dozens of reactions or even more. “Our model is a purely theoretical concept, a signal indicating that a part of the phenomena occurring during somitogenesis are controlled by truly simple mechanisms”, stresses Assoc. Prof. Nowakowski.

Having in hand a theoretical model describing the dynamics of a phenomenon observed in embryogenesis, the Polish-French team was able to verify the effect of internal noise on the described process.

In nature, the noise is a consequence of the discrete, molecular structure of matter, an unavoidable, stochastic effect occurring in every physical system. In a theoretical model, noise can be introduced or suppressed at will. This also means that the theoreticians can do what the experimentalists cannot: to compare a naturally non-existing noiseless system with a noisy system – and to assess the effect of thermodynamic fluctuations on the segmentation process.

“Usually, one assumes that an accidental noise disturbs the existing order. Our simulations gave an opposite result. After the noise has been introduced into the model, periodic patterns started to appear significantly faster, just after the chemical wavefront has passed”, describes Assoc. Prof. Nowakowski. The thermodynamic fluctuations turned out to accelerate the formation of the periodic spatial pattern and to stabilize it in time. Moreover, the system formed easier the patterns, in a clearly broader range of parameter values.

The research has been carried out under the Polish-French Polonium Program, and the results are published in the Europhysics Letters journal.
The tools used to detect chemicals are an indispensable companion in chemist’s work, but find also numerous applications outside the laboratory’s walls. Continuous improvement of the detection methods is extremely important. Their growing sensitivity, accuracy and selectivity are of key importance for the development of science and industry.
INTERNATIONAL SURFACE METROLOGY STANDARDS

Superficial layers of materials, no thicker than several atomic layers, play a key role in many important areas of science and technology, including microelectronics, nanotechnology, catalysis or corrosion science, material engineering and many other areas. These surface layers are nowadays being studied with different surface sensitive techniques, in particular with electron spectroscopies.

Quantitative surface analysis by spectroscopic methods requires taking into consideration certain parameters that are available in the databases distributed by the US National Institute of Standards and Technology (NIST) in Washington. Several of these databases, commonly used by researchers worldwide, are being developed by Prof. Aleksander Jabłoński from our Institute.

The surface of materials determines the way they interact with the environment. The presence of impurities can, however, change the surface in a hardly predictable manner.

“Even when a material contains alien molecules on a few parts per million level, they can migrate to the surface and cover the whole sample. Surface properties of such a substance are then different than those of the material’s interior”, says Prof. Jabłoński, stressing that the knowledge on actual physical and chemical properties of materials’ surfaces is of paramount importance to industries employing the most recent accomplishments of material engineering, microelectronics and various nanotechnologies.

Surface studies employ usually two research methods: photoelectron spectroscopy and Auger electron spectroscopy. In the former, the surface of the sample is irradiated with X-rays and the electrons ejected by photons from surface layers are recorded. In the latter, the material is bombarded with a monoenergetic electron beam, and the energies of electrons emitted due to intra-atomic radiationless transitions (i.e., transitions not accompanied by photon emission) are recorded. As only the electrons ejected from atoms close to the surface have a chance to leave the sample without energy loss, both methods “see” only a few most external atomic layers of the material.

Prof. Aleksander Jabłoński (left) at the multichamber spectrometer during visit of ambassador of Japan. (Source: IPC PAS, Grzegorz Krzyżewski)
The photoelectron spectroscopy allows to analyze the valence and the chemical form of elements, as well as the distribution of chemical compounds on the material surface, including non-conductors such as substances of biological origin, ceramics or plastics. An electron beam can be focused easier than the x-rays and therefore the Auger electron spectroscopy allows for a better resolution of the element distribution on the surface, approaching in the most recent instruments 10 nanometres.

Accurate analyses by surface sensitive spectroscopies imply necessarily a development of a reliable theory of electron transport in surface region of condensed matter. The mathematical formalism describing the phenomenon is founded on certain parameters that allow a quantitative surface analysis.

Extension of theory accomplished by Prof. Jabłoński and his proposals of new parameters resulted in a development of comprehensive databases making life easier for electron spectroscopy users. These compilations – containing parameters such as electron scattering cross sections, mean free paths of electrons and electron attenuation lengths – attracted interest of the US National Institute of Standards and Technology that subsequently started to distribute them. As a result, in years 2001-2010 more than 2000 software packages containing databases developed in our Institute have been distributed. Recently, Prof. Jabłoński has completed tests of another database, SRD 154, which includes so-called modified backscattering factors.

For his work on how to increase the accuracy of surface analyses using spectroscopic techniques, including the preparation of databases for the NIST, Prof. Jabłoński has been awarded with the prestigious Maria Skłodowska-Curie Scientific Award. The award is awarded annually by the Division III Mathematical, Physical and Chemical Sciences of the Polish Academy of Sciences, alternatively in physics and in chemistry. The award is presented to Polish scientists, non-members of the PAS, whose outstanding and creative work particularly contributed to the development of science.
INNOVATIVE SENSOR TO DETECT MELAMINE CONTAMINATION

Utilisation of molecular imprinting process allowed our researchers to construct a unique chemical sensor (chemosensor) for selective detection of melamine. The substance is sometimes used illegally to artificially increase the protein content in food products that is measured with detectors examining the amount of nitrogen in a sample.

“Our method for detecting and determining melamine concentration allows for a measurement accuracy that so far could be reached in laboratories only”, says Prof. Włodzimierz Kutner. After laboratory tests, a patent application for the device was filed.

Melamine became ill-reputed after a scandal with Chinese milk. In second half 2008, melamine came up in dairy products manufactured in China, including baby nutrients. Melamine-contaminated products were found later in shops worldwide, including Germany and Slovakia. Health problems were diagnosed in 300,000 individuals, 50,000 babies were admitted to hospitals, six of them died.

Melamine is used in industry in manufacturing polymer materials used in production of glues, kitchen countertops and dishes, chemical fertilisers and dyestuffs (it must not be mistaken with melanine, a dye responsible for, e.g., the colour of the iris). After entering human body, melamine in combination with cyanuric acid – a detergent used in sterilising food packaging – forms yellow concrements in renal tubules leading to serious health problems; in extreme case they can even lead to death.

Until present precise melamine assays could be carried out in laboratories only. “Food industry used indirect methods consisting in determining the nitrogen content in a sample. The choice of nitrogen was not accidental, as the element occurs mainly in proteins”, explains Prof. Kutner.

Melamine contains very large amounts of nitrogen: it accounts for as much as 2/3 of its mass. Therefore, in China it was commonly added to milk diluted with water. Sensor readings showed high nitrogen content in products, which in turn suggested high nutritional value of the samples.

“The detector developed at our Institute does not respond to nitrogen but directly to melamine. When a tested solution flows through the detection layer of our chemosensor, only melamine molecules fit molecular cavities and only they can be entrapped”, describes Prof. Kutner.

The detection layer is deposited on an electrode of a quartz resonator. When melamine molecules are filling the cavities, the mass of the layer increases, resulting in a changed frequency of resonator oscillations. After measurement, melamine molecules can be washed out and the sensor can be used again.

The key element of the chemosensor is a few hundreds nanometer thick detection layer. The layer is produced using the molecular imprinting technology. Melamine is mixed with a functional monomer, whose molecules surround melamine molecules. Then another (cross-linking) monomer is added and copolymerised with the functional monomer. Melamine molecules are washed out from the emerging hardened polymer structure. The result is a porous three-dimensional sieve with cavities capable of anchoring melamine molecules only.

In cooperation with the Institute of Physics of the PAS our scientists initiated research aiming at elimination of the quartz resonator from the design, as the component is very sensitive to the chemosensor’s conditions of operation. It could be replaced by semiconductor transistor structures. Their base areas can be coated with detection layers of molecularly imprinted polymers. Utilisation of these structures will open the way to commercialisation of the invention.

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Dr Piotr Pięta at a prototype of a selective melamine sensor developed in our Institute under the “Quantum semiconductor nanostructures” project. The key sensor’s component is an appropriately designed molecular sieve. (Source: IPC PAS, Grzegorz Krzyżewski)
POLYMER’S HUNT FOR NICOTINE

The collaboration of researchers from the Department of Chemistry, Wichita State University (WSU) and our Institute has resulted in fabrication of a polymer trap for nicotine. Bearing molecular pincers, the newly synthesized polymer effectively captures nicotine molecules and its analogues, and can also release them in a controlled way. The compound will be used in reusable chemical sensors for determination of nicotine for industrial and biomedical purposes as well as for therapeutic purposes, e.g., in patches for smokers to evenly release nicotine to the body for a prolong time.

“The first nicotine trap has been synthesized by our US partner, Prof. Francis D’Souza, several years ago. It was a sort of molecular pincers, molecules that freely move in solution and form complexes with nicotine therein. Recently, our US-Polish team has been able to fix the pincers inside a polymer. The substance is solid, and that’s why we could use it to construct chemosensors”, says Prof. Włodzimierz Kutner (IPC PAS).

The core of the polymer nicotine trap, which has been recently filed for a patent, is a metalloporphyrin derivative,

Fitted with molecular pincers, the polymer synthesized in collaboration between the Wichita State University and our Institute allowed fabricating a chemical sensor for determination of nicotine in solutions. The picture shows Dr Eng. Krzysztof Noworyta. (Source: IPC PAS /Grzegorz Krzyżewski; picture by courtesy of the Warsaw’s Fajka Bar)
a substance present, i.a., in human blood. The molecule contains a ring (a macrocycle) with a centrally located zinc atom and amide pincers attached to this ring. Nicotine binds to this polymer with its two nitrogen atoms: one binds to the zinc atom, whereas the other to the pincers.

“It is due to the specific two-point binding that we are surer that the captured molecule is nicotine”, stresses Dr Krzysztof Noworyta (IPC PAS), adding that in one of the devised polymers the pincers are located on both sides of the zinc containing-ring plane. “Such a design clearly increases the efficiency of nicotine trapping”, says Dr Noworyta.

Beside nicotine, the polymer captures also a cotinine alkaloid produced in the metabolism of nicotine and other alkaloids often accompanying nicotine, e.g., myosmine. Polymer binding to nicotine is durable but reversible. It is the property why the new chemo sensors for determination of nicotine and its analogues can be used repeatedly.

Nicotine is detected by means of a piezoelectric resonator coated by electropolymerization with a submicrometer thick polymer film. The captured nicotine increases the mass of the film resulting in a decrease in the resonant frequency of the resonator that is easy to measure.

“It can be said that we are weighing a film of our polymer all throughout the experiment. Because we know the initial polymer mass and we know that the polymer selectively captures nicotine and its analogues, an increased mass of the film means that these compounds are present in solution”, explains Dr Noworyta.

Quartz acoustic bulk wave resonators used in experiments with the new polymer allow determining nicotine in solutions. In the near future, the researchers from our Institute plan to establish collaboration with manufacturers of surface acoustic wave resonators. These resonators oscillate at significantly higher frequencies, thus being more sensitive, and after coating with the nicotine capturing polymer film could detect nicotine also in gases.

In the method described herein, the detection and determination of nicotine do not need to be confined to weighing. Because nicotine is electroactive, our researchers are going to measure oxidation current of nicotine trapped in the polymer in parallel with the resonant frequency measurement. Simultaneous measurement with these two methods will increase the detection reliability.

The polymer with pincers for nicotine can be used, among others, in chemo sensors devised to analyze nicotine content in tobacco leaves and in biomedical studies to determine nicotine metabolites in patients’ body fluids. Another potential application are nicotine patches to help quit smoking. The new polymer could be used for prolong and smooth release of nicotine.

On the Polish side, the research described herein has been performed within the project “Quantum semiconductor nanostructures for applications in biology and medicine”. The project, funded in 85% from the European Regional Development Fund, has been awarded to seven Polish research institutions for construction of prototype diagnostic devices on semiconductor substrates, designed for applications in biology, medicine, and environment protection as well as for the development of fundamentals of materials technologies for sensor applications and molecular diagnostics devices. Almost 50 researchers from our Institute participate in the project implementation.
Laboratory on a microchip, capable to detect most types of antibodies in patient’s blood in a single test, would be a revolutionary breakthrough in medical diagnostics. The physicians would gain rapid access to examined patient’s personal health records with the data on both past and present diseases, as well as those that will develop only in future.

This unusual vision gets closer to reality due to innovative, gold-coated gallium nitride substrates with specifically formed surface, developed by researchers from the Institute of High Pressure Physics of the PAS (IHPP PAS) and our Institute. Worldwide unique properties of the substrates open for the first time the way to long expected dissemination of surface enhanced Raman spectroscopy (SERS), a technique capable of detecting bacteria, viruses, and even single molecules.

Surface Enhanced Raman Spectroscopy is an exceptionally attractive analytical tool yielding powerful enhancement of the original signal, usually from million to billion times. Thanks to the new substrates, it has finally got a chance – after decades of waiting in specialized laboratories – to widespread and revolutionize medical diagnostics.

“Lack of substrates with appropriate nanostructures has, for last three decades, prevented SERS application in medicine. We managed finally to overcome the obstacle”, says Prof. Robert Hołyst (IPC PAS).

Substrates with roughness features in nanometer scale play a key role in Raman spectroscopy. The Raman effect is the inelastic scattering of photons on molecules. Usually a light scattering molecule absorbs a photon and immediately emits another one with the same energy – the phenomenon is termed by physicists elastic or Rayleigh scattering.

Sometimes it happens, however, that a part of photon energy is transferred, e.g., into vibrations or rotations of a molecule. Then, the photon emitted by the molecule will have slightly lower energy. An opposite situation can also happen: the molecule will give some energy to the emitted
photon. In both cases the scattering is known as Raman scattering, after the name of its discoverer, Indian physicist and Nobel Prize winner Chandrasekhara Venkata Raman. The scattering is an extremely rare phenomenon: only one photon per dozens of millions is scattered in that way, which means it is very hard to detect.

In 1974, British chemist Martin Fleischmann with co-workers observed an unusually strong Raman scattering signal from molecules placed on a roughened silver substrate. Further studies revealed that the enhancement effect is real and occurs also on substrates made of gold, platinum and copper. In each case, the necessary condition for enhancement to occur was an appropriate surface morphology.

"If the surface is appropriately roughened, the electromagnetic field intensity on sharp edges of surface unevennesses is significantly increased. For a similar reason, all spire structures attract thunderbolts", explains Prof. Holyst.

The molecules deposited on so prepared surface are in a very strong electromagnetic field and much more frequently scatter photons inelastically via Raman scattering.

A good SERS substrate should have rather regular, periodic surface structure assuring that the signals recorded by the measurement setup are reproducible. Its design is based on gallium nitride (GaN) substrate, developed in the Institute of High Pressure Physics of the PAS.

"The manufacturing starts with fabrication of a GaN substrate covered evenly with structural defects of nanometer size", says D.Sc. Janusz Weyher from IHPP PAS. The surface is then photoetched, the process takes place everywhere except for the defects and results in formation of vertical pillars with approximately the same diameters. Due to tension forces, free terminals of adjacent nanopillars attach to each other, forming numerous structures resembling stacks in the field. At that stage, the substrates are transferred to our Institute, where a thick gold layer is evaporated on to them. The process yields a surface coated with an even thicket of nanometer size golden cones.

SERS substrates designed by Polish researchers have unique properties. "The substrates commercially available so far had to be handled with extreme caution. They had to be stored under nitrogen, could not be touched and even though they were loosing their enhancement ability within hours only. Our substrates can be put into an ordinary drawer for a couple of months and they will be still usable", stresses Dr Agnieszka Michota-Kamińska (IPC PAS).

For economic reasons, it is important that our substrates are suitable for multiple use as the only ones worldwide. Their surface structure is so stable that our research-
GOLD MICROFLOWERS TO ENHANCE SIGNALS FROM MOLECULES

Surface Enhanced Raman Spectroscopy (SERS) is a promising research tool that allows to enhance signals emitted by molecules by hundreds of thousands or even millions of times. “There is, however, no joy without annoy”, says Assoc. Prof. Marcin Fiałkowski. “To reach so high enhancement, the molecules must be placed on an appropriately shaped substrate. Under electron microscope, such substrates resemble peaked mountains, like Alps for example. The difference is that here the peak heights are measured in nanometres, and the mountains are covered not with snow but with a layer of gold”.

At present no cheap, good and easy-to-use substrates for SERS analyses are available on the market and this is one of the factors inhibiting commercialization of the method. A promising solution to the problem seem to offer substrates developed recently at our Institute under the research project “Quantum nanostructures”.

The highest enhancement of a SERS signal is obtained when a molecule is placed in the meeting area of two “peaks” of the substrate. The effect can be hardly reached with existing mountain-like surfaces, as the peaks there are distinctly separated.

The new substrates from our Institute are fabricated by depositing spherical, strongly ragged gold structures precipitating from solution, on a slide surface. When observed under electron microscope, these micro-

Katarzyna Winkler, a PhD student, reviews electron microscope images showing substrates fabricated with gold microflowers. (Source: IPC PAS/Grzegorz Krzyżewski)
meter-sized spheres resemble flower buds composed of many gold petals.

„When ragged microflowers are deposited on the surface, they form thick, complex 3D structures with numerous meeting areas between the petals. That’s why the signals emitted from our substrates are enhanced even by ten million times”, stresses Katarzyna Winkler, a PhD student.

Equally crucial as the enhancement is the repeatability of signals obtained from a specific substrate. In that respect the layers of gold microflowers show excellent performance. The signals originating from molecules of the same type that are placed at different locations on the same substrate are very similar to each other, and this is not always the case for surfaces obtained with other methods. High signal repeatability has also been observed for substrates fabricated on various slides, using separately prepared solutions.

The fabrication of substrates using gold flowers is fast, simple and cheap, does not require to use neither robots nor clean rooms. „The reaction mixture contains only a gold salt and a reducing agent, mixed in an appropriate mixing ratio. The role of the reducing agent is to reduce gold cations to metallic gold”, says Winkler. What remains is to immerse a roughened slide in so prepared solution. The deposition of gold flowers is usually completed within one hour, and the substrate is ready for use on the next day.

The method of covering surfaces with gold microflowers designed for SERS applications has been filed for patenting. The present goal of the researchers from our Institute is to develop substrates that can be used repeatedly in measurements involving various analytes. For that purpose, methods to wash out analytes while leaving the substrate structure intact are being developed.
CARBON NANOSTRUCTURES FOR DETECTION OF PARKINSON’S DISEASE

Dopamine deficiency is indicative of serious diseases of the nervous system. Tests of dopamine concentration – being usually very low in physiological fluids – are expensive and require specialised equipment that is unavailable in doctor’s offices. This situation may change due to a recent invention from our Institute.

Our researchers have developed new electrodes coated with carbon nanoparticles deposited on silicate submicroparticles. The electrodes have been successfully applied to determine dopamine concentration in solutions in the presence of uric and ascorbic acids, and paracetamol, the substances interfering with dopamine analysis.

The developed method of dopamine detection opens the way to low cost and quick medical tests that could be used by physicians in their offices to determine with high likelihood if a patient suffers from popular nervous system diseases, such as Parkinson’s disease.

The electrodes developed at our Institute are composed of alternate layers of silicate submicroparticles and carbon nanoparticles. The silicate submicroparticles are from 100 to 300 nanometer (billionth parts of meter) in size. As non-conductive, they are used only as a framework extending the electrode surface. The silicate particles are densely coated with carbon nanoparticles (from 8 to 18 nm in size) that form the actual conductive working surface.

“Carbon nanoparticles have negatively charged functional groups, and the silicates positively charged ones. The electrostatic interactions between them are quite strong. We checked that by multiple repeating of the immersion a ‘sandwich’ consisting of up to 24 layers can be obtained on the electrode surface”, describes Anna Celebańska, a PhD student.

The researchers from our Institute have applied the new electrodes for dopamine sensing in solutions. Dopamine deficiency is characteristic for, i.a., Parkinson’s disease and therefore the detection of the deficiency is of essential medical importance. This, however, is not simple, as dopamine concentration in body fluids, even in healthy individuals, is very low. Moreover, samples containing dopamine usually include other compounds such as uric and ascorbic acid. Both compounds generate signals similar to those produced by dopamine, and they are present at thousand-fold higher concentrations.

To test dopamine concentration using the new method, the electrodes with carbon nanoparticles are immersed in an appropriately prepared solution containing the sample, and then electric potential is applied. Dopamine is electrochemically active and can be oxidised by appropriately adjusting the potential value.

Unfortunately, dopamine signal is usually masked by signals originating from ascorbic and uric acids. The carbon nanoparticles on the electrode surfaces change, however, the potential values at which both acids are oxidised. Consequently, the peaks in the plot are separated and the signal from dopamine becomes visible.

“The results of the completed tests turned out very
good. Our method is among the most sensitive methods for dopamine sensing. It allows to detect dopamine at concentrations as low as $10^{-7}$ mole per liter in the presence of interferences at concentrations up to $10^{-3}$ mole per liter”, says Celebańska.

The present methods of dopamine sensing are expensive and require specialized equipment, but at the same time relatively cheap, palm-size instruments for detection of chemicals are available on the market. If they would be equipped with new electrodes and popularized in doctor’s offices, a patient might learn about his/her illness before leaving the doctor’s office.

Dopamine sensing with new electrodes is possible down to concentrations corresponding to those in body fluids of a healthy individual. Lower concentrations that are characteristic for sick individuals will not be precisely determined and the detector will not work.

“The method has a natural detection threshold, and that’s why we can conclude on dopamine deficiency in the body. How large is the actual deficiency? At present we cannot answer the question. We hope, however, for further increase in the method’s sensitivity”, states Prof. Marcin Opałło.

The electrodes coated with carbon nanoparticles deposited on silicate spheres allow detecting dopamine deficiency in the presence of interfering substances. They can be used to diagnose popular diseases of the nervous system. Pictured above: Anna Celebańska, a PhD student and the first author of a publication describing new electrodes. (Source: IPC PAS, Grzegorz Krzyżewski)
WALKING MICRODROPLETS COLLECT VIRUSES AND BACTERIA

A barely visible, electric-field-controlled droplet moves on an appropriately prepared surface, harvesting viruses, bacteria and protein molecules deposited thereon. This is how a novel method of collecting bioparticles looks like in real life. The method has been for the first time successfully tested by a team of researchers from the French Institut d’Electronique, de Microélectronique et de Nanotechnologie (Dr Vincent Thomy), the Institut de Recherche Interdisciplinaire (Dr Rabah Boukherroub) and our Institute (Dr Martin Jönsson-Niedziółka). The results of the tests will have an impact on the development of microsystems for chemical analyses, especially those dedicated to monitor bioparticles present in the air.

The future of chemistry are miniaturised devices designed to carry out reactions and chemical analyses. The fabrication of such systems, popularly called “labs on chip”, is seriously challenging the engineers.

“You can make an excellent microfabricated analytical system, but to make it work you still have to prepare the sample in a proper way”, says Dr Martin Jönsson-Niedziółka (IPC PAS/Grzegorz Krzyżewski)

Methods of surface cleaning by removing bioparticles using electric-field-controlled microdroplets has been developed by Dr Martin Jönsson-Niedziółka. (Source: IPC PAS/Grzegorz Krzyżewski)
Assume we have viruses and bacteria on a surface. Would we try to simply wash the surface with water, and then introduce a droplet of that water into a microanalyser, the result would be poor. Just because the concentration of the pollutants will be too low.

To ensure the highest possible concentration of bioparticles, it is better to use a small water droplet, just a microliter in volume. Such a droplet is introduced between two plates: a lower one with pollutant particles earlier deposited electrostatically, and a top one, coated with a system of small electrodes and an insulating layer (protecting against current flow through the droplet, which could lead to electrolysis).

By making use of a phenomenon called electrowetting and applying voltage in a proper way, the droplet can be precisely displaced over the surface and so collect bioparticles from the entire plate. An additional advantage of the method is that the sample collected is already in the liquid state as required by many measurement methods. Moreover, as the displacement of the microdroplet is easy to control, the problem of how to deliver the sample to further lab-on-chip components disappears.

The systems with microdroplets have been fabricated and tested for a couple of years. The international research group with our scientists had doubts about the fact that all earlier reports on microdroplets described the collection of latex microspheres from the surface. These particles are used because they are easily available in various sizes and safe in tests. It was not clear if the microdroplets would equally efficiently collect real bioparticles, such as bacterial spores or viruses.

The study made use of a microdevice fabricated by the French group. The particles investigated in tests included inactive bacteriophage MS2 (virus that infects bacteria), *Bacillus atrophaeus* spores and OA (ovalbumin) proteins.

The bioparticles were deposited on two different surfaces. One of them was a hydrophobic surface, coated with a substance that resembles Teflon. The other plate was fabricated using nanowires (1 micrometer long) and its hydrophobicity was close to that characteristic for the famous lotus leaves. Until now, such superhydrophobic surfaces were not studied in any microdevices making use of electrowetting.

In experiments with viruses, the type of surface they were deposited on did not have any significant effect on the microdroplet cleaning efficiency. The cleaning efficiency was 98-99% and was higher than that typical for latex particles (92-93%). Different results have been found, however, for spores and protein molecules. High cleaning efficiency was found here for superhydrophobic surface only (99 and 92%, respectively), whereas the corresponding figures for hydrophobic surface were distinctly lower (46% and 71%, respectively).

The findings, published in the prestigious journal “Lab on a Chip”, demonstrate that the surface cleaning efficiency using microdroplets strongly depends on both the type of collected particles and the hydrophobic properties of the surface.

“Everyone who wants to collect efficiently various bioparticles using microdroplets should use superhydrophobic surfaces”, sums up Dr Jönsson-Niedziółka.
CHEATING GELS

How one gelator molecule can immobilise as much as a few thousands of solvent molecules? Comprehensive understanding of the mechanism responsible for gel formation may open the way to the development of new materials and safer transportation methods of liquids that pose a risk to the environment. The structure of gels, however, can hardly be studied directly, as proven by experiments carried out at our Institute.

Imagine two fully loaded oil tankers collide at a harbour entrance. Is then a massive environmental disaster unavoidable? Today, the most likely answer is: yes. In future, the collision may result in a twisted metal only. The oil will not get out because inside the tank it will have a form of a gel.

“Transportation of dangerous liquids in a gelled form is now a fantasy. It can not be excluded, however, that the future will bring gelling agents allowing for increased safety. To make it happen we have first to get a deeper insight into the internal structure of gels and the mechanisms of gel formation”, says Dr Roman Luboradzki.

Gels are systems resembling more or less elastic jelly in appearance. Typically, they are two component systems: one component plays the role of a solvent whereas the second one acts as a gelator. In the gelling process (consisting in cooling down liquid mixture of both components), the gelator develops an extensive network in the gel space that immobilises the solvent. The network is mostly composed of amorphous structures resembling fibres or ribbons, and more rarely spherical structures in touch with each other.

In chemical gels, gelator molecules attach to each other through strong covalent bonds, forming very rigid and durable structures. Physical gels, such as those studied at the IPC PAS, are formed following another principle. The gelator, usually an organic substance, contains small molecules composed of over a dozen to a few tens of atoms (that’s why they are called: Low Molecular Mass Organic Gelators, LMOG). The molecules assemble to form long structures via weak noncovalent interactions including hydrogen bonding, pi-pi stacking, van der Waals forces, etc.

The transition of a physical gel into a liquid and of a liquid into a gel are reversible processes. Usually, the transitions are very fast, and
occur by changing temperature by only 1-2 degrees nearly the critical value.

The analysis of gel structures, especially those of LMOG type, is difficult. Both gel components have often similar transparency and the structural details of the network are not larger than from over a dozen to a few tens of nanometers in size. A gel with such structure can not be examined under an optical microscope. And the scanning electron microscopy (SEM) requires to place a sample in vacuum. This requirement translates into a special preparation procedure of a gel sample for microscopic examinations.

Typically, researchers use two methods to guarantee that the structure of a gelator is preserved under a SEM microscope. The first one is to place the sample in a vacuum pump. Under lowered pressure the solvent quickly evaporates leaving a fixed gelator that typically looks like a white powder. The resulting structure is called xerogel. Xerogels are also produced using sublimation. In this method, the sample is rapidly frozen in liquid nitrogen. It is usually assumed that freezing of the sample occurs so fast the structure of the network formed by the gelator does not change. The frozen sample is then placed in a vacuum chamber where the solvent gradually sublimes.

"The problem is that some SEM images show crystals in xerogels that theoretically should not be present there. We didn’t know if the crystals are a real part of the gel structure or rather a side-effect of the gel preparation procedure for microscopic studies. That’s why we decided to check how the xerogel structure changes with time and as a function of the method used to prepare samples for microscopic studies", says Dr Luboradzki.

The results obtained at our Institute indicate that not always a SEM image corresponds to what is the original gelator structure in a gel.

A necessary step of the sample preparation procedure for SEM studies is to evaporate a conductive layer on top of the sample. As the sample was locally warmed up in the process, the researchers were afraid that it may lead to changes in the xerogel structure. The evaporation tests with carbon, platinum, gold and palladium have shown, however, that the evaporation has no effect on the xerogel morphology.

The researchers managed also to notice that the structure of some xerogels was dependent on the volume of the sample, and even on the shape of a vessel containing the sample. Xerogels prepared in a standard bottle contained more crystalline structures than the samples with volume ten times less but placed in capillaries.

It was also observed that the transformation of amorphous fibres of finished gel into crystalline form could be speeded up by slightly warming up the sample. Moreover, after few months some xerogels developed spontaneous crystallisation. This means that even a properly prepared xerogel sample can essentially change its structure before it is placed in a SEM microscope.

"Xerogels are playing unfairly with researchers – at least some of them are trying to cheat us. Now, being aware of that, we can avoid many misinterpretations and faster solve the riddle of how one small gelator molecule can efficiently bind even ten thousand solvent molecules", says Dr Luboradzki.
NEW METHOD OF CHEMICAL ANALYSIS
Information on how strongly two dissolved substances react with each other is very important in many fields, in particular in chemistry, molecular biology, pharmacy and medicine. The new simple analytical technique, developed at our Institute, allows the inexpensive and reliable determination of stability of complexes created as a result of reactions between chemical compounds in solutions. What is interesting, the measurement involves very simple physical phenomena and comes down to the examination of the flow of a solution of two compounds in a long and thin tube – a capillary.

Every angler knows that rivers flow fastest in the middle part of the stream, and near the banks the current is always slower. A liquid flowing through a capillary behaves in a similar way. If the flow is nonturbulent (laminar), the layers of the fluid that are closest to the centre of the capillary flow faster than the layers near the walls.

“This is the fact that we use in our method, but the key are phenomena connected with diffusion”, said Dr Anna Bielejewska.

In reality, particles of a liquid may move (diffuse) from a layer flowing with a certain speed to another layer flowing with a different speed. If we insert a substance into a capillary filled with the solution of another substance, the diffusion rate will depend on how strongly the chemical compounds of both solutions react with each other. If particles move quickly between the layers, a detector will register a high and narrow peak. The slower the particles diffuse between layers, the wider the peak.

“If we measure the width of the peaks before and after the introduction of a complexing agent into the capillary, we can determine the diffusion coefficients of a free substance and a complexed substance, and on this basis calculate a binding constant. It provides information whether given chemical substances bind with each other or not, and if yes, how permanent the bond is”, explains Dr Bielejewska.

The device developed in our Institute comprises a pump which guarantees the stable flow of the liquid at 0.05 millilitre per minute, an autosampler inserting a sample, a detector of visible and ultraviolet radiation and a 0.25 mm diameter capillary, 25 m long, wound around a small cylinder.

The obtained results of measurement agreed perfectly with the data collected by classical chromatographic methods and figures cited in international scientific publications. In one of the numerous tests conducted, the capillary was filled with the solution of diluted blood plasma, which contains protein (albumin), after which warfarin, an organic chemical compound used as an anticoagulant, was injected. In this case the results of the experiment were also correct.

The new analytical technique, for which a patent application has already been submitted, may be applied not only in chemistry but also in medicine for the selection of dozes of medicines whose concentration in blood should be strictly determined.

“At present a physician first prescribes a medicine to a patient, then takes a blood test and, if something is wrong, changes the doze, checks again and this procedure is repeated until it succeeds. Thanks to our method it will be possible to take several millilitres of blood once before the treatment and determine how strongly the blood binds a given medicine and what doze should be applied in order to obtain the concentration in the body that would be optimal for the treatment”, said Bielejewska.

A single analysis using new method lasts approximately half an hour. After this time appropriate software would provide the physician with a result in the form of a doze of medicine adapted to specific features of a given patient’s organism.

“We have developed a new, efficient method for the analysis of chemical reaction equilibrium in solutions, for which cheap and simple measurement equipment is required. It is up to the industry whether the method becomes widespread”, comments Prof. Robert Holyst.

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New method of analysis of chemical reaction equilibrium consists in the examination of the flow of a liquid in a long and thin tube – a capillary. In the photo there is a PhD student Paulina Dobosz standing next to a liquid chromatograph, with a capillary in her hand. (Source: IPC PAS, Grzegorz Krzyżewski)
...TO MAKE USE!

The power of a really good science lies in its applications. Science translating into problems of everyday life not only enables further technological and scientific advancement of the civilisation, but also creates a favourable social climate for its own development.
LABORATORY IN MICRODROPS

A group of our scientists, headed by Assoc. Prof. Piotr Garstecki, constructed a microfluidic device allowing the streams of drops containing various solutions to merge. The new system makes it possible to produce and precisely control concentrations of reaction micromixtures, and it operates several times faster and with smaller volumes of liquids than the microtitre plate method currently popular at laboratories. “The device developed by us will allow even tens of thousands of biochemical experiments to be conducted daily”, says Assoc. Prof. Garstecki. The microlab may significantly affect the manner in which experiments are carried out with respect to chemical synthesis and medical diagnostics and biotechnologies.

The microflow system constructed in our Institute is a miniature chemical reactor with the size of a credit card. Reactions proceed inside tiny drops moving along specially designed, small channels. Volumes of the drops are controlled with the use of a computer and are usually equal to approx. one microlitre. The system can work at a speed that allows mixing three drops per second. Additionally, instead of microvalves which it is difficult to construct, scientists used inexpensive typical big valves which they placed outside the device.

“Miniaturisation of everything is simply not economical. Taking the valves outside the micro-system, the chip itself can be made simple, cheap and disposable. The most im-
Important thing is that the chemical reactions themselves proceed in a microscale under precisely controlled conditions”, explains Krzysztof Churski, a PhD student.

The invention of our researchers has already got a potential to significantly influence the development of numerous areas of chemistry and medicine, in particular screening. Currently, screening is carried out with the use of microtitre plates – plates with several hundreds of wells filled in by a robotic handler. In this type of research cost of a single reaction reaches approx. three dollars, but the value of reagents is approx. 20 cents; the remaining part is the cost of maintenance of apparatus and its infrastructure. Since in a typical project to search for a new drug the number of tested compounds ranges from several hundreds to as many as several millions, the costs can reach millions of dollars. “Our microflow system not only reduce all costs but also significantly shortens the time necessary to conduct research”, emphasises Assoc. Prof. Garstecki.

The microflow system made by our scientists may be particularly useful in looking for new medicines, especially composed of several antibiotics. Pairs of antibiotics usually have stronger (synergistic pairs) or weaker (antagonistic pairs) effect than each of their components individually. However, it is particularly interesting that certain antagonistic pairs show high effectiveness in fighting microorganisms, which cannot be easily predicted. The existing laboratory methods allow for description of such pairs but demand conducting a huge number of labour intensive experiments. The apparatus constructed at our Institute can quickly identify the interesting pairs of antibiotics that could prevent one of the basic problems of modern medicine – the creation of drug-resistant strains.

Tests conducted by our researchers allowed to demonstrate the operation of the microflow system in the conditions simulating the run of automated screening. Each microdrop merged with two microdrops of antibiotics, chloramphenicol and tetracycline, and the volumes of the former two were changed dynamically, which regulated the proportions between the drugs. The drops mixed in the microflow system were left for three hours in order to incubate bacteria. Then the intensity of light emitted by metabolism markers was analysed, which allowed vitality of colonies in individual drops to be easily determined. The entire process was automated and showed that the mixture of the antibiotics examined is the least effective where the proportion of the components is equal.

Microflow techniques are seen as the future of chemical engineering. They go back to the 1990s when the works on the first systems of channels began. At that time, liquids with chemical reagents were let through the channels with diameters of a tenth or hundredth of millimetre. Where small volumes are used, the flow is laminar and it is subject to effects related to viscosity, which makes it easier to control the run of the reaction (macroscale flows are often dominated by inertia and turbulence).

Systems producing drops are simple and inexpensive, substances in microchannels mix very well and their flow is usually caused by the difference in pressure, i.e. a physical phenomenon that does not influence the chemical composition of a liquid (contrary to, for instance, flows that are caused by an electric field). In future the volume of drops can be reduced to nanolitres or even picolitres. Many scientists agree that microflow systems will change the nature of modern chemistry as dramatically as integrated circuits changed electronics in the 1970s.
Small droplets in emulsions can merge much faster in the presence of an alternating electric field. The phenomenon, used industrially in large scale applications, is called electrocoalescence and is of essential importance for the operation of advanced microfluidic devices, allowing one to carry out chemical reactions in microliter volume or less. A recent study carried out at our Institute, financed from a TEAM grant from the Foundation for Polish Science and the Iuventus-Plus Programme of the Polish Ministry of Science and Higher Education, allows for improved control of electrocoalescence and for optimisation of the course of the process.

Electrocoalescence has been known for over 100 years. Originally, it has been used in the oil industry. Crude oil extracted from the sea floor contains significant amount of water in a form of droplets. Engineers have noticed that in the presence of an alternating electric field these droplets merge quickly and fall on the tank bottom from where the water can be easily removed.

“Electrocoalescence has started its career untypically, from large scale applications in the oil industry. In microfluidics the phenomenon has been applied to merging of droplets only within the last few years”, says Assoc. Prof. Piotr Garstecki.

Examination of changes in the rate of microdroplets merging as a function of parameters of external electric field. The picture shows Tomasz Szymborski, a PhD student, at work in the lab. (Source: IPC PAS/Grzegorz Krzyżewski)
Microfluidic devices are miniaturised chemical reactors resembling a credit card in size. Chemical reactions take place inside the droplets that are suspended in a neutral liquid flowing through appropriately designed microchannels. The droplets can be very small: from a fraction of a microliter even down to nano- or picoliters.

“The primary challenge in microfluidic techniques is to combine the stability of droplets with the ability to merge them. Stabilization requires covering the interface with a surfactant, i.e., a surface active agent”, explains Tomasz Szymborski, a PhD student.

Surfactant molecules are composed of a hydrophilic (water-loving) and a hydrophobic (water-hating) part. If a water droplet is placed in oil, the surfactant covers it so that the hydrophilic parts are immersed in the droplet, whereas the hydrophobic ones remain in oil.

“From outside, the droplets covered with surfactant resemble rolled up hedgehogs and have no chance to touch each other. Their stability is increased due to the fact that surfactant molecules repel each other via electrostatic and entropic forces”, explains Szymborski.

Problems appear when precisely selected droplets of different reagents are to be merged in a microfluidic device to carry out a chemical reaction. Since recently electric field has been used to induce merging. Electrocoalescence is known for its macro scale industrial applications, yet how the mechanism and efficiency of the process depends on the parameters of the electric field was largely an open question.

The researchers at our Institute observed merging of water microdroplets in a carried liquid, hexadecane. The rate of droplet merging increased in line with applied voltage and the frequency of electric field oscillations. For each voltage there was a limiting frequency, above which the droplets became stable again.

“We showed that the merging proceeded at its maximum rate when the electric field oscillated with a frequency close to a threshold one and we found a simple function allowing to estimate the value of the threshold quickly”, says Szymborski.

Rapid merging of droplets is related, i.a., to a periodic movement of ions contained in the droplets that are stimulated by an alternating electric field. The ions separate in the oil-droplet interface while charging it electrically. The droplets with opposite charges attract strongly, which results in droplet merging in spite of the presence of stabilizing surfactants. The results of the study suggest that there is a simple relation between the nanoscopic electrostatic screening length and the optimum frequency for merging of droplets.

The data collected by our researchers will be helpful for practical optimisation of processes involving electrocoalescence, both in microfluidic devices and industrial plants. The results will also facilitate formulation of universal laws describing the efficiency of electrocoalescence in non-equilibrium systems such as flowing liquids.
SIMPLE WAY TO SEPARATE NANO-POLLUTANTS

We live in the age of dynamic development of various nanotechnologies. A side effect of their popularisation is the fact that more and more nanometric structures get into the environment. Many of these structures are very dangerous for man. Carbon nanotubes may be of length similar to the size of a cell – more than ten micrometers – with a diameter of just several nanometres; such an object acts like a needle and it is hard to remove it from the body. Nanostructures that have a round shape, made of hazardous materials, e.g. cadmium selenide particles, are also dangerous. Meanwhile, methods of mechanical and chemical treatment of sewage do not eliminate nano-pollutants, whereas laboratory methods are successful only in the case of little volumes of liquids.

Our Institute developed an innovative sewage treatment process allowing nanometric size pollutants to be separated. The process can be used on an industrial scale. “The solution turned out to be so simple, cheap and effective that it is already protected by four patents”, emphasises Prof. Robert Hołyst.

The method for the separation of nanometric particles, developed within the last five years, consists in adding to the polluted solution two substances: surfactant (i.e. surface active agent, such as soap) and polymer (e.g. inexpensive and environment-friendly PEG). “If we match concentrations properly, all tiny pollutants will gather in the upper, floating layer with consistency of thin soap, under which there is clean water with polymer which can be easily recovered”, says Assoc. Prof. Marcin Fiałkowski. The upper layer of the surfactant can be collected by mechanical methods in a simple way, and then it can be utilised or processed in order to recover the substances it contains.

The physical mechanism responsible for the separation of the substance in the solution is connected with the difference between geometrical sizes of surfactant and polymer particles. Surfactants – substances that are dominant components of all cleaning agents – create in solutions aggregates called micelles. They can have various shapes but they often look like ordinary balls. Polymer, on the other hand, has a form of a ball of wool, which also resembles a ball. If two “balls” of a surfactant get close enough to each other, the smaller “ball” of polymer will not be able to squeeze between them and will remain at a certain distance, called radius of gyration. Therefore, when micelles of a surfactant approach each other and the distance between them is smaller than twice the radius of gyration, an empty space is created between them. This results in a difference in concentrations of polymer and osmotic pressure related to this difference. Water flows out from among micelles, they get closer and within several dozens of minutes phases in the solution become separated. The process occurs even when charged polymer of the same sign is added into the solution containing ionic surfactant.

The research showed that if there were any particles in the original solution, they gathered in the layer rich in surfactant.

“During one of the experiments we studied a solution of gold nanoparticles which had the size of five nanometres. After several percent of soap and approx. 10% of polymer had been added, a viscous and elastic layer with a surfactant was created on the surface. It contained particles of gold which, being heavier than water, under different conditions should fall down to the bottom”, describes Ewelina Kalwarczyk, a PhD student from the Department of Soft Condensed Matter. The method is effective also in the case of detergents that become denser and are raised to the surface.

It is particularly important for the application of this method on an industrial scale that upon the completion of the process, polymer remains in water from which it can be nearly completely recovered. The only substance that is used up fully is the surfactant, i.e. soap, in which nano-pollutants are closed. Tests which lasted 11 months did not show any changes in the physical and chemical stability of the surfactant collected, which means that the particles contained in it are effectively isolated from the environment.

Surface layer being created in solutions has an orderly hexagonal structure. Since the type of the order depends only on concentration, structures of this type are called lyotropic liquid crystals. Thanks to the method being described, carefully selected nanoparticles can be easily introduced into matrices that form the structures. The matrices can be fixed and the organic part can be removed. Therefore, the method developed in our Institute can be used not only to treat sewage but also to produce composite materials containing admixtures of gold, platinum, silver, semiconductors, carbon nanotubes, etc. This type of materials can be used for the construction of solar cells and various types of catalysts, e.g. car catalysts.
Ewelina Kalwarczyk, a PhD student, with a sample in which fluorescent semiconductor nanoparticles were separated. (Source: IPC PAS/Grzegorz Krzyżewski)
SEPARATION THOUSAND-FOLD FASTER
Inhomogeneous blends of polymers with other polymers or liquid crystals are widely used in industrial applications – in LCD displays, gas-flow sensors, optical memories and other devices. Researchers from our Institute have studied how the external electric field affects the rate of component separation in blends composed of polymers and liquid crystals and those composed of various types of polymers.

“We managed to determine precisely the conditions permitting even a thousand-fold acceleration of component separation process in the blends under study”, says Prof. Robert Hołyst. The observations gathered open interesting opportunities, e.g., for the development of new composite materials.

With time, many blends separate spontaneously into their components, usually at a very low rate. It has been known since long that the separation can be accelerated when an inhomogeneous liquid is placed in an external alternating electric field with adequately tuned frequency. It is generally accepted that the acceleration of separation is due to ions – natural constituents of such mixtures.

The researchers from our Institute studied blends of a polymer with another polymer or liquid crystal. In the presence of an alternating electric field with the strength of several million volts per meter the ions of the component with higher conductivity start to move freely towards the electrode with the opposite charge. Having reached the phase interface with a non-conductive material on the other side they are strongly hampered.

“Under these conditions, an additional force appears at the interface. With electric field alternating at appropriate frequency the ions start to yank the interface. Due to the yanking, the droplets of a component merge with each other significantly more efficiently than in the normal case, thus leading to a faster separation of both phases”, says Natalia Ziębacz, a PhD student.

The separation efficiency of studied blends into their components is strongly dependent on the frequency of the applied electric field. Optical measurements carried out at our Institute have shown that under optimal conditions, at frequencies up to the kilohertz range, the separation takes place even thousand-fold faster. Too low or too high frequencies of the electric field do not result in significant movements of ions and the separation occurs at a regular, low rate. The physical mechanism of the phenomenon suggests that similar effect can be expected in all blends contaminated with ions and containing components with different charge conductivities.

Controlling the rate of separation process over so long time range, extending over three orders of magnitude, opens the way to interesting applications. The separation process can be carried out very quickly, and then virtually stopped at a precisely selected stage. The structure of the blend so obtained can be then fixed, for instance by changing the temperature. Thus, the method to control separations of blends of polymers and liquid crystals using electric field turned out to be an excellent tool for the development of new materials. A patent application for the method has been filed.

The research presented here has been financed from grants provided by the Polish Ministry of Science and Higher Education, the TEAM Programme of the Foundation for Polish Science and the European Science Foundation.
SOLAR ALCHEMY

In many places of the world water is highly polluted by organic chemicals from industrial wastes. Polluted water can be easily cleaned and treated to extract valuable chemicals, e.g., used in drug manufacturing. No factories or plants are needed, the sun and a “magic” powder are enough. The nearly alchemic transformation is accomplished due to photocatalysts studied by our researchers.

The experiments carried out at our Institute prove that the biomass can be successfully transformed into useful chemicals and fuel. Due to appropriately selected photocatalysts, the transformation of polluted water into clean one and chemicals does not require specialized plants and takes place under conditions that are commonly met in nature.

Catalyst is a substance that participates in the chemical reaction, speeds its course and fully recovers after the reaction is completed. In typical catalytic processes the catalysts are activated at high temperatures, typically of several hundreds degrees centigrade, often at a significantly increased pressure.

“Photocatalysts studied by us differ in many respects from traditional catalysts. They are activated by light, and the temperature has no significant effect here”, says Dr Juan Carlos Colmenares. The reactions with participation of photocatalysts occur at good exposure to sun rays, at temperature about 30 degrees centigrade and at normal atmospheric pressure – so at conditions occurring naturally all year round in many equatorial countries.

The photocatalysts studied at our Institute are solids based on titanium dioxide, TiO₂. The catalysed reaction occurs in a liquid containing organic pollutants. After the reaction is completed, the catalyst can be isolated almost without losses and used again.

“My work resembles somewhat alchemy”, jokes Colmenares. “I take a ‘magic’ powder, pour it into polluted water, stir and expose to the sun. After several hours, I get clean water plus chemicals that can be used to make useful things, for instance drugs”.

The research on photochemical degradation of pollutants has been carried out in the world already in the late 1960’s. By intensive UV irradiation chemical compounds with simple structures have been obtained at that time.

The research pursued at our Institute aims at such a selection of photocatalysts and reaction conditions that the reaction can occur without using specialized equipment, and the degradation of biomass stops at a precisely defined stage.

With titania-based photocatalysis the researchers managed to produce carboxylic acids used, e.g., in pharmaceutical and food industries. It is also possible to prepare a photocatalyst so as to have the reaction completed and yielding substances with the simplest structure, such as hydrogen or carbon dioxide. The latter compound is undesirable and would require disposal, hydrogen, however, has excellent prospects as the fuel of the future.

“In laboratory conditions, the reactions of the biomass with participation of photocatalysts are promising already now. Soon we are going to attempt the first tests in the pilot biochemical photoreactors at the University of Cordoba, Spain. The reactions will occur there in liquids with volumes measured in tens of litres”, says Colmenares while making clear that still many tests and studies are to be carried out before the new technology gets disseminated.

The co-authors of the paper published in the “Bioresource Technology” journal, describing application of photocatalysts to glucose degradation and to production of valuable chemicals, are Agnieszka Magdziarz and Dr Anna Bielejewska. The research has been financed from an international Marie Skłodowska-Curie reintegration grant under the 7th Framework Programme of the European Union.
ARTIFICIAL WHITE LIGHT BECOMES EYE-FRIENDLY

A new class of organic substances, discovered by scientists from the Faculty of Chemistry of the University of Warsaw and our Institute, emits white light with continuous spectrum. This achievement provides experimental evidence that only single component luminophore will be necessary to construct eye-friendly light sources and displays. An article on the discovery of white fluorescence was published in “Physical Chemistry Chemical Physics” journal.

Tired eyes and the impression that white is artificial are known to everyone who spends time in places lighted by popular non-thermal sources like fluorescent lamps or LEDs. Scientists from laboratories all over the world have been trying to eliminate these unpleasant side effects for years in their search for methods to recreate the sun light which is the most natural light for humans. In our Institute it was shown that this objective could be achieved.

“We have discovered a class of organic molecules emitting white light with continuous spectrum covering almost the entire visible range”, says Assoc. Prof. Jerzy Karpiuk who heads the research team. It is also important that the emission of the white light was obtained from one chemical compound with a very simple structure.

White is a special colour which is created as a result of mixing of light waves of all lengths from the visual range, i.e. from approx. 420 to approx. 730 nanometres (one nanometre is one billionth part of a meter). The white colour of fluorescent lamps and similar artificial sources is created by the mixture of three colours only: red, green and blue, which come mainly from the non-continuous emissions of various inorganic (halophosphate or triphosphate) luminophores. The light obtained in this way is devoid of many colour components and it is this effect that is responsible

White fluorescence in CVL molecules continuously covering practically the entire range of visible light. The discovery shows that in future it will be possible to create non-thermal light sources giving the impression of natural white colour, based on single component luminophore. (Source: IPC PAS, Grzegorz Krzyżewski)
for the unpleasant visual sensations. In addition, the need to use several substances lowers the energetic efficiency of light sources and complicates their manufacturing technology.

The research team – Jerzy Karpiuk (IPC PAS), Ewelina Karolak (IPC PAS) and Jacek Nowacki (Faculty of Chemistry of the University of Warsaw) – observed white light emission continuously covering virtually the entire visible range. Its source is crystal violet lactone (CVL), a substance produced in mass quantities and commonly used in copy paper as the so-called dye precursor.

A CVL molecule has two fluorophores embedded in its structure and responsible for the emission of light: one for blue and the other one for orange. The contribution of each of them to CVL’s dual fluorescence heavily depends on the environment of the molecule which modifies the energetics of their excited states. “By properly adjusting the molecule’s surrounding, it is possible to control the parameters of the emission spectrum, and consequently, to change the colour or shade of the white light obtained”, says Ewelina Karolak, a PhD student.

“The deeper significance of our research lies in the discovery that white fluorescence is a general property of CVL type molecules. The dependence of excited state energetics on molecular structure allows to predict the width, shape and other parameters of the dual fluorescence spectrum, and so enables the engineering and customised design of white fluorophores”, adds Assoc. Prof. Karpiuk.

It turns out that even very small molecules can emit continuous white light. This fact opens up a new perspective for the construction of innovative eye-friendly light sources.

The emission of white light by molecular structures as simple as CVL is highly desired and wanted phenomenon, mainly because of its potential use in organic light-emitting diodes. However, it is still a long way before it can be used in practice because crystal violet lactone emits light of low intensity and CVL-based light sources would not be efficient enough to be manufactured on a mass scale.

“The most important thing is that we managed to show that a certain concept works in practice. Now we are sure that it is only a matter of time before light sources recreating natural white light will be constructed”, Assoc. Prof. Karpiuk sums up the discovery.

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Considered by many as the most promising material of the future, graphene still remains an expensive and hard-to-fabricate substance. Researchers from the Interdisciplinary Research Institute in Lille and our Institute developed a low cost method for manufacturing multilayered graphene sheets. The new method does not require any specialized equipment and can be implemented in any laboratory.

Graphene was discovered in 2004, by peeling off carbon layers from graphite using an ordinary scotch tape. “In what had been peeled off the researchers were able to find one-atom-thick sheets. And that was graphene. If we are thinking about industrial applications of graphene, we have to find better controlled methods for producing this material in a large scale, without using an expensive, specialized equipment”, says Izabela Kamińska, a PhD student from the IPC PAS, a scholarship holder of the Foundation for Polish Science within the International PhD Projects Programme.

Kamińska has carried out her experiments at the International Research Institute.

Considering the structure, graphene is a two dimensional system composed of six-membered carbon rings. The hexagonal graphene lattice resembles a honeycomb, with the difference that the graphene sheet has the lowest possible thickness: of one atom only.

Unusual properties of graphene are closely related to the unique structure. Graphene is almost entirely transparent, more than hundred times stronger than steel and very flexible. At the same time it shows excellent thermal and electric conductivity, which makes it a good material for applications in electronics, e.g. for manufacturing thin, flexible and strong displays or fast processing circuits. It is also suitable as a material for various sensors.

The existing methods for fabricating graphene – including deposition of epitaxial layer on a metallic substrate...
or silicon carbide, or chemical or physical vapour deposition – require expensive, specialized equipment and complex manufacturing procedures. Meanwhile, the only more complex apparatus used in the method for producing graphene sheets developed at the IPC PAS and the IRI is an ultrasonic cleaner, an equipment common in many laboratories.

The new process for producing graphene sheets starts with graphite, one of carbon allotrope, on the molecular level resembling a sandwich composed of many graphene planes. These sheets are hardly separable. To weaken interactions between them, graphite must be oxidized, which is usually accomplished with the Hummers method. A powder obtained in that way – graphite oxide – is subsequently suspended in water and placed in an ultrasonic cleaner. The ultrasounds exfoliate oxidized graphene sheets from each other and the resulting colloid contains single graphene oxide flakes with diameter of about 300 nanometers.

The researchers from the IPC PAS and the IRI used graphene oxide manufactured at Materials Science Division in North East Institute of Science and Technology (NEIST) in Dispur, India.

“One-atom-thick graphene oxide colloids were a good starting material, but numerous oxygen-containing functional groups became a real difficulty. The problem was that they changed dramatically the physico-chemical properties of the material. Instead of an excellent conductor we had... an insulator”, explains Kamińska.

To remove oxygen from graphene flakes, the researchers decided to use non-covalent pi-pi stacking interactions between the carbon rings of graphene oxide and the aromatic rings of a compound called tertathiafulvalene (TTF). A TTF molecule is composed of two rings containing three carbon and two sulphur atoms each.

“Practically, it was sufficient to mix graphene oxide with tertathiafulvalene, and then put the whole in an ultrasonic cleaner. The interactions between the TTF rings and the graphene oxide rings resulted in a reduction of graphene oxide to graphene with a simultaneous oxidation of the TTF molecules”, describes Kamińska.

As a result, the obtained composite contained graphene flakes with TTF molecules intercalated into them. A droplet of the composite solution was subsequently deposited onto an electrode and dried. Graphene flakes formed on the surface a smooth coating with controllable thickness from 100 to 500 nanometers that was composed of a few dozen to a few hundreds alternate graphene sheets and TTF molecules.

The final stage in the production of graphene coating was to expel tertathiafulvalene molecules, which was attained by a simple chemical reaction with an appropriately selected compound.

“One of our motivations for the research was to look for new methods for detecting biological substances. That’s why after expelling TTF from the graphene coating we checked immediately if we could reincorporate the chemical into the matrix. It turned out that yes. Therefore it is possible to develop a process allowing one to bind a selected compound to a TTF molecule, and then to incorporate the entire complex into a graphene sheet on an electrode and monitor the electric current flow”, sums up Prof. Marcin Opałło (IPC PAS).

A publication describing the new method appeared in the prestigious journal “Chemical Communications”, with the cover showing computer visualisation of the graphene sheets with TTF. At present, the researchers from the IPC PAS and the IRI continue their work on further decrease of graphene matrix thickness. The final stage reached also the experiments which show that it is possible to incorporate into the graphene sheet TTF molecules with attached mannose (one of the monosaccharides).
RED LIGHT FROM CARBON NANOTUBES

The researchers involved in the international FINELUMEN project, coordinated by Dr Nicola Armaroli from Italy’s Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche (CNR-ISOF) in Bolonia, have developed an efficient method to fabricate a new photonic material: carbon nanotubes coated with chemicals that are capable of displaying red light.

To the human eye, carbon nanotubes usually appear as a black powder. They can hardly be forced to emit light, as they are excellent electrical conductors and capture the energy from other luminescent chemical species placed nearby.

“We take part at the project as a research group specializing in studies on lanthanide compounds. We decided to combine their high luminescent properties with excellent mechanical and electrical characteristics of nanotubes”, says Prof. Marek Pietraszkiewicz (IPC PAS).

Carbon nanotubes can be envisaged as a graphite sheet rolled-up into a seamless cylinder. The surface area of each nanotube is relatively high and allows to attach many other molecules, including those capable to emit light. Attachment of light-emitting complexes directly to the nanotube is, however, not favourable, because the latter, as a black absorber,
would highly quench the luminescence", explains Valentina Utochnikova, a PhD student at the IPC PAS.

To reduce undesired effect of light absorption, the nanotubes are first subject to a thermal reaction at temperature 140–160 °C in a solution of ionic liquid modified with a terminal azido function. The reaction yields nanotubes coated with molecules acting as anchors-links. On one side the anchors are attached to the surface of the nanotube, and on the other they can attach molecules capable of displaying visible light. So prepared nanotubes are subsequently transferred into another solution containing a negatively charged lanthanide complex – tetrakis-(4,4,4-trifluoro-1-(2-naphtyl)-1,3-butanedionato)europium.

“Lanthanide compounds contain elements from the VI group of the periodic table and are very attractive for photonics, as they are characterised by a high luminescence quantum yield and a high colour purity of the emitted light”, stresses Utochnikova.

After dissolving in solution, negatively charged europium complexes are spontaneously caught by positively charged free terminals of anchors attached to nanotubes due to electrostatic interaction. As a result, each nanotube is durably coated with molecules capable to emit visible light. Upon completion of the reaction, the modified nanotubes are washed and dried. The final product is a sooty powder. If the powder is, however, exposed to UV irradiation, the lanthanide complexes anchored to nanotubes start immediately to emit red light.

The concept of how to modify the nanotubes and the reagents – ionic liquid and lanthanide complex for carbon nanotube coating – has been developed in Prof. Pietraszkiewicz’s research group, whereas the modification of nanotubes and spectral studies have been performed by research groups from the University of Namur, Belgium, and CNR-ISOF from Bolonia, Italy. It is essential that chemical reactions leading to fabrication of new light-emitting nanotubes turned out to be significantly simpler than those used so far.

The photonic material received can be used, among others, to detect molecules including those of biological importance. The identification would then take place by analysing how the luminescence of nanotubes changes upon deposition of molecules under study thereon. Good charge conductivity combined with high luminescence properties make new nanotubes an attractive material also for OLED-based technologies.

The international FINELUMEN project is implemented as a training action for young researchers of the Marie Curie Initial Training Networks, under the 7th EU Framework Programme.

The issues related to new photonic materials, including luminescent nanotubes, were among the topics of two recent Summer Schools organized in 2011 by the Institute of Physical Chemistry of the PAS and the Polish Supramolecular Chemistry Network Foundation: “FINELUMEN” International Summer School in Łochów (http://fiss2011.pl/) and VIII International Krutyń Summer School (http://ikss2011.pl/). The Krutyń Summer School’s main subject were advanced photovoltaic technologies, and the third School’s co-organiser was the University of Edinburgh.
UNUSUAL LIQUID CRYSTAL STRUCTURES ON WATER SURFACE

After pouring on a water surface, liquid crystals can form ordered layers of monomolecular thickness. When compressed from sides, such films can wrinkle like fabric on a flat, smooth table, pulled together with palms simultaneously from both sides. With increasing surface pressure, the wrinkles of the monolayer fold up and form subsequent layers. The research on new compounds has resulted in the discovery of new mechanisms of multilayer formation that are responsible for creation of liquid crystal films with a structure that has never been observed before.

When monolayers of liquid crystals are compressed in their plane, they can form, under appropriate conditions, a film composed of three layers – a trilayer. It was supposed that from time to time even 5-layers may be formed. “The existence of 5-layers has not, however, been well documented. We managed to confirm their presence with high precision. Moreover, we observed 9-layers that until now were considered exclusively as research suggestions”, says Dr Andrzej Żywociński. The research findings have been published in “Chemistry – A European Journal”.

Our researchers poured microliters of liquid crystals on the surface of water. The compounds and their amounts were adjusted so as to form an ordered monomolecular layer (with a thickness of one molecule). The monolayers can be compressed with an apparatus called Langmuir trough. It is basically a trough with two hydrophilic barriers, between which a monolayer of chemical compound under study is drifting on the water surface. By reducing the distance between the barriers one can significantly increase the pressure in the monolayer plane.

The research pursued by Dr Żywociński and Prof. Robert Holyst’s PhD students was focused on about a dozen compounds from the group of bolaamphiphiles synthesised in Prof. Carsten Tschienske’s research team from the Martin-Luther-University of Halle-Wittenberg. The molecules of these compounds have various complicated shapes, sharing a rigid core with hydrophilic (water-loving) groups attached to both ends. These groups anchor the molecule to the water surface. In addition, the central part of the core contains hydrophobic (water-hating) chains. A part of molecules studied had two hydrophobic groups in an X-shaped arrangement, another part – one such group in a T-like configuration, while in the remaining molecules the core was not straight but bent, resembling the shape of an anchor.

In molecules used in the study, hydrogen atoms in hydrophobic chains were partially replaced with fluorine atoms, which resulted in an increased rigidity and hydrophobicity. Due to the substitution, the molecules, especially those X-shaped, formed on water very stable, well ordered monolayers.

The measurements have shown that the molecules of compounds studied behave somewhat like fabric on a table (with one significant difference: a fabric is solid, and the processes described here occur only if the compound is in the liquid phase). When a monolayer is compressed from sides, the forces acting in the system displace the molecules upward, and the monolayer develops folds that subsequently roll over. If the compression is continued, an ordered structure composed of three monolayers is formed on the water surface. The process has already been described in the scientific literature.

“We were able to observe and document a much more interesting mechanism”, says Jan Paczesny, a PhD student from our Institute. “It turned out that further compression of a trilayer formed by one of the compounds leads to the folding that involves not one, external monolayer, but the entire trilayer. The fold being pushed out has then a thickness of six layers and after rolling over on a trilayer, our molecular ‘fabric’ becomes an excellently ordered 9-layer”.

An increase of the multilayer thickness in the sequence: mono-, 3- and 9-layer was suggested in the literature, but the mechanism was for the first time confirmed experimentally.

The group from the IPC PAS studied also substances, where the intermolecular interactions were not sufficiently flexible. During compression of such compounds, it is not the monolayer that folds and rolls over, but single molecules are pushed out over the monolayer and after detachment from water surface aggregate in pairs. Being non-volatile, they stay with the monolayer and are ordered with increasing pressure, forming at once two layers on the monolayer. This newly recognised mechanism explains why multilayers increase their thickness in sequence 1-3-5-7 monolayers.

The researchers are convinced that processes similar to the both observed ones occur also for other chemical compounds with similar molecular structure.

Practical application of the ordered multilayers is possible after transferring them from the water surface onto a solid substrate, e.g. silicon wafer. To do so, a silicon wafer is
repeatedly immersed and removed from a bath consisting of water with a multilayer. Unfortunately, the monolayers of some substances are being washed out during repeated immersions. Our researchers met such situation for one of the compounds studied. The measurements have shown, however, that the same compound is transferred permanently when a 9-layer is formed. This means not only that a new type of substrates can be produced but also that the time required to form thick multilayers that were previously produced by laborious deposition of up to a few dozen monolayers can be nine-fold reduced.

The cores of molecules studied in our Institute have three condensed aromatic rings. Analogous structures appear in conducting polymers. "We hope that in future the derivatives of the compounds studied by us will find an application in organic electronics. We also plan to make use of the tendency for self-organisation of these molecules to organise other molecules", comments Dr Żywociński.

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The roll-over mechanism of liquid crystal layers on the water surface, responsible for formation of the 9-layer film, is presented by Dr Jan Paczesny. (Source: IPC PAS, Grzegorz Krzyżewski)
PREPARATION OF THIN FILMS OF NANOPARTICLES
Glass and semiconductors coated with uniform thin film of nanoparticles find more and more applications. Researchers at our Institute have developed two methods for preparing gold monolayers – coatings as thin as a single nanoparticle. One of them makes use of surprising properties of highly concentrated salt solutions, while the other is based on self-assembly. Both methods allow preparing for the first time uniform, positively charged monolayers.

In contact with water, glass and silicon surfaces may spontaneously generate a negative electric charge. Deposition of thin and uniform layers of positively charged gold nanoparticles from solution on such surfaces seemed impossible so far. The nanoparticles aggregated and instead of developing a uniform layer, they formed numerous clusters. To decrease the effective range of electrostatic interactions between the nanoparticles, chemists have usually added salt to the working solution. The salt anions shielded in part the nanoparticles, which then could deposit more densely.

"The solution is far from ideal, as the more salt we add the entire system is getting more destabilized. As a result, at certain level of salt concentration the nanoparticles start to precipitate from solution in a form of aggregates", notices Katarzyna Winkler, a PhD student. It was commonly believed that the phenomenon was an insurmountable obstacle.

"We decided to check how the nanoparticles would respond if we increase the salt concentration in spite of all. And here we faced a surprise", says Winkler.

The researchers from our Institute have noticed that in certain range of high salt concentrations the working solution regains stability and the nanoparticles in the solution stop to aggregate while still being able to interact with the substrate.

"Most likely we are dealing with an electrostatic effect. The discovery, however, is so fresh that the exact nature of the phenomenon has not been recognised by us", says Assoc. Prof. Marcin Fiałkowski.

In the second method for preparing uniform nanoparticle coatings on substrates the key role is played by self-assembly. Gold nanoparticles were first covered with thiols – RSH type molecules containing an R substituent and a group composed of one sulphur S and one hydrogen H atom. In experiments, electrically charged hydrophilic thiols and uncharged hydrophobic ones were used. Nanoparticles surrounded by the thiols were then placed on a water surface.

"If we properly adjust the proportions between charged and uncharged thiols, the nanoparticles present on the water surface start to behave like floats. They don’t sink, but form spontaneously a monolayer”, describes Dr Volodymyr Sashuk.

A layer of nanoparticles formed on water surface due to self-assembly can be compressed mechanically with an apparatus called Langmuir balance. As a result of compression, the nanoparticles, even when covered by thiols with the same charge, approach each other to a much shorter distance.

"Now, to transfer such a monolayer on a glass substrate it’s enough to make use of the Langmuir–Blodgett method. To do so, a glass plate is placed in a computer-controlled dipping arm and slowly immersed in water or raised above the surface. Then, the nanoparticles from the surface layer just attach to the plate", says Dr Sashuk.

As the direction of the plate displacement through the monolayer decides which side is the one the nanoparticles use to attach to the glass, the method allows preparing hydrophobic or hydrophilic surfaces. Moreover, it is possible to cover glass surfaces with monolayers of either negatively or positively charged nanoparticles – just depending on what is needed.

The first of the above methods is very simple, and also very cheap. It can be used when the charge and order of nanoparticles do not matter. The recipe allows to form layers not only on glass but also on semiconductor substrates. With the method one can fabricate, for instance, silicon surfaces coated with gold nanoparticles that in further processing would initiate growth of nanowires. Self-assembly based production of nanoparticle layers is more complicated. The layers obtained are, however, highly ordered, and their electric charge can be precisely controlled.
CARBON NANOOBJECTS FOR FUTURISTIC POWER SOURCES

Scientists from our Institute are working on the electrodes that have surfaces covered with layers of carbon nanoparticles and enzymes. These electrodes can be used to produce modern sensors and power sources, including such futuristic ones as biological fuel cells installed inside human body and fueled by substances contained in blood.

One of the most popular methods of covering surfaces with nanoparticles is the Layer-by-Layer method (LbL) known...
since 1997. According to this method, a substrate is covered with subsequent layers of objects with opposite electric charges. This method is applied in particular to create three-dimensional structures made of polymers only or alternating layers of polymers and nanoparticles on the surface of electrodes.

“From some time it has been known that many electrode reactions proceed faster, more efficiently and selectively on surfaces covered by, for instance, nanoparticles of gold or carbon. So, we decided to construct structures consisting of nanoparticles only and examine how they affect the properties of electrodes after they have been further modified by enzymes”, says Prof. Marcin Opałło.

Electrodes covered by thin layers of carbon nanoparticles could be applied to, among other things, biological fuel cells used as sources of power for medical devices placed in human body. Currently, the replacement of power sources in such devices like pacemakers requires invasive methods. For years, all over the world works have been carried out, aimed at creating a cell fuelled by a substance dissolved in blood, for example, glucose and an oxidizing agent – oxygen, which is also in blood.

The task is difficult because a conductive support must be found which will allow the permanent deposition of enzyme in such a way that it would exchange electrons directly with the electrode. This was finally achieved in our Institute thanks to depositing carbon nanoparticles on the electrode.

“The result is surprising, because enzyme usually requires additional compounds – electron shuttles dissolved in the solution. There are simply no such compounds in our experiments”, says Katarzyna Szot, a PhD student.

It is particularly important that the electrodes being examined work in the solutions that have similar components as blood plasma.

Carbon nanoparticles used in the experiments carried out in our Institute are smaller than 10 nanometers. In the context of future applications it is important that they are cheap and easily accessible.

“At first, we wanted to buy nanoparticles but it turned out that such small quantities that we needed are not traded. For example, Mercedes uses such nanoparticles on a mass scale to paint car bodies. Eventually, we received one kilogram of the material, free of charge, from Cabot Corporation”, laughs Prof. Opałło.

The process of covering the substrate – in the experiments these are glass plates with a layer of an electric conductor – is simple and quick. The plate is immersed for one minute in the suspension of carbon nanoparticles, then it is taken out, rinsed, moved to another suspension to deposit a subsequent layer, and all the actions are repeated several times. The finished carbon layers are about 100 nanometers thick.

As carbon nanoparticles themselves are small, spaces between them are also very small, which makes the access to active surfaces located deeper in the layer more difficult. As a result the electrodes are not as efficient as they could be. In the future it will probably be possible to improve their properties due to the modification of the process of layer depositing.

The experiments in our Institute are just beginning on the application of carbon nanoparticles layers in the presence of small polystyrene balls with diameters of several hundred nanometers. After each layer has been created, scientists intend to coat it with polymer in order to strengthen the structure mechanically and then wash away the balls. The multi-layer structure obtained thanks to this method would have larger pores facilitating access of oxygen, which would result in the increased reaction efficiency.

Electrochemical sensors will probably become another area where electrodes with carbon nanoparticles layers can be applied, e.g. to determine the level of dopamine in relation to ascorbic acid and uric acid. This problem is considered serious in analytical chemistry since the two last substances hinder the analysis of samples due to the overlapping of their electrochemical signals. Covering the electrodes with nanoparticles allows the signals to be separated and sensitivity to be increased.

In addition to carbon nanolayers, scientists from Prof. Opałło’s team create, in a similar way, three-dimensional structures from nanoparticles of metals and metal oxides, carbon nanotubes and nanoparticles of modified glass.
In scientific laboratories and industrial plants nearly all chemical reactions take place in liquids, but a group of scientists from the Faculty of Chemistry of Warsaw University of Technology (FC WUT) and our Institute managed to produce an interesting chemical compound through the reaction which was conducted in a solid only. During the research it was also discovered that the grinding of the new compound, even in an ordinary mortar, led to the creation of cubic molecular structures.

“This last result is particularly astonishing”, comments Prof. Janusz Lewiński (IPC PAS, FC WUT). “By using simple mechanochemical methods we managed to change one complicated three-dimensional molecular structure into another, also three-dimensional, and, what is most interesting, surprisingly regular structure. This is the first mechanochemical reaction of this type in the world”.

The discovery was described in an article published in a prestigious chemical journal “Angewandte Chemie”.

Mechanochemistry consists in running chemical reactions in solids, which in practice comes down to grinding powders. Chemists knew that trituration was important for a long time, but it was supposed that the reason was the change in the proportion between the surface and the volume in lumps of the substance grinded. However, at the end of the previous century crystallographers noticed that grinding also caused changes in the structure of organic...

The grinding of powders in a mortar can result in chemical reactions during which regular three-dimensional molecular structures are formed. In the photo there is Michał Dutkiewicz, a graduate student from the Faculty of Chemistry of Warsaw University of Technology. (Source: IPC PAS, Grzegorz Krzyżewski)
compounds. This is possible because these compounds form crystal structures with weak non-covalent bonds. During the trituration the bonds break and new chemical compounds are created.

“Mechanochemical reactions run very quickly and in the entire volume of powders. If we put, for instance, two white powders in appropriate proportions in a mortar or a shaker, after just several dozens of minutes we can pour out yellow powder which will be a new clean chemical compound”, explains Daniel Prochowicz, a PhD student (FC WUT).

Since during the grinding of biologically active compounds new crystal structures – polymorphic varieties that may be patented – are obtained, pharmaceutical industry has become strongly interested in mechanochemistry in recent years.

A starting point for the reactions discovered by our scientists was a compound containing complexes of zinc oxide ZnO, in which atoms of zinc are bound weakly by molecules of a solvent. At the temperature of 35 °C the compound was subjected to lowered pressure. This caused desolvation, that is the molecules of the solvent separated from metal complexes. X-ray analysis revealed that an alkyl-alkoxy zinc compound was created as a result, with a unique complex spatial structure which cannot be obtained by any other method.

Since the substance produced by our scientists is a precursor of zinc oxide, it can be used to produce this semi-conductor commonly used in electronics. What is more, thanks to the unique spatial structure of the compound, nanoparticles of zinc oxide obtained from that compound have slightly different properties than ZnO nanoparticles produced with the use of other methods, and consequently, they can have new applications in various types of nanotechnologies.

The compound created during desolvation turned out to be a trimer, which means that each of its molecules comprises three basic units – mers. These mers form a surprisingly complex and asymmetric spatial structure. The new compound of zinc, in the form of powder, was grinded manually in a mortar. On the basis of X-ray analysis of the substance obtained as a result of grinding it was possible to state that it was not a trimer anymore but a tetramer with a very regular, cubic crystal structure.

The result was a considerable surprise for the researchers. Earlier mechanochemical transformations with the use of complex compounds either changed the structure of the complex or resulted in the creation of a coordination polymer, that is a one-dimensional metal-metal chain connected by organic links.

“We managed for the first time to cause a mechanochemical transformation of a cluster into another cluster, that is to go from one three-dimensional structure to another one”, says a student Michał Dutkiewicz (FC WUT). The physicochemical mechanism responsible for this astonishing transformation remains unknown.

The discoveries of our scientists open the way to the synthesis of new groups of alkoxy compounds that are precursors of oxide compounds. This type of compounds is widely used, in particular in electronics and material chemistry, including many nanotechnologies.

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PHEROMONES AS A MEANS TO PROTECT BEECH FORESTS

European hardwood ambrosia beetle poses a threat both for living beech populations and cut wood. Until now, foresters had no pheromone-based agents allowing them to monitor and reduce the population of this pest. A new pheromone compound, developed at the CHEMIPAN R&D Laboratories of our Institute, turned out to be efficient not only in attracting the European hardwood ambrosia beetle but also other beetle species from the Trypodendron genus. The substance has been developed on the order of the Austrian company Witasek Pflanzenschutz GmbH and field-tested in forests in Germany.

“The results of the tests carried out by our German colleagues turned out to be an exceptionally pleasant surprise”, says Assoc. Prof. Jerzy Raczko, CHEMIPAN’s managing director.

Pheromones are volatile substances secreted by living organisms to their environment for communication purposes. They play various roles: usually they indicate the presence of the female or the abundance of food, but are also used as warning signals. Attracting properties of pheromones have since long been used by foresters to fight insects. Pheromone traps allow them to monitor, reduce or fight specific pest population.

“Pheromones occur naturally at extremely low concentrations, and that’s why using them is exceptionally environment-friendly and economic. For instance, each year we provide foresters in whole Poland with several dozens of thousands of pheromone traps to monitor the black arches population. All the traps contain only 12 grams pheromone in total”, explains Assoc. Prof. Raczko.

European hardwood ambrosia beetle (Trypodendron domesticum, Xyloterus domesticus) is a small, dark beetle, cylindrical in shape and not longer than four millimeters. It occurs mainly in beech populations, especially in the damaged ones, where it infests birches, oaks, maples, limes and other deciduous trees. Most Poland’s forests are pine monocultures, where the primary threat is the striped ambrosia beetle (Trypodendron lineatum, Xyloterus lineatus) feeding on conifers.

“For years we have had chemicals to effectively attract the striped ambrosia beetle. Now, we used them as a basis to develop a new pheromone, tailored to attract the European hardwood ambrosia beetle”, describes Assoc. Prof. Raczko.

The field tests have been carried out by researchers from the Technical University of Dresden in the tree populations near Leipzig, Dresden and Wermsdorf. The forests comprised common beeches, oaks and ashes. To the our researchers surprise, not only European hardwood ambrosia beetles and striped ambrosia beetles were observed in high, mutually comparable numbers in pheromone traps, but also the bark beetle (Trypodendron signatum, Xyloterus signatus). Test results indicate that the new agent is efficient against all beetles from Trypodendron genus.

Ambrosia beetle infests deciduous trees, mainly beeches, oaks and ashes. (Source: Robert Dzwonkowski)
The pheromone-based agent attracting the beetles will allow for better determination of dates when these pests start and culminate their swarming. Measurements with traps will contribute to a more efficient monitoring of the tree populations and allow the foresters to take preventive measures at appropriately early time, which in turn will result in reduced damages of insect infestations.

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RECORD-BREAKING LASER

Dr Yuriy Stepanenko at the optical table with a laser setup. (Source: IPC PAS, Grzegorz Krzyżewski)
In the Laser Centre at the Institute of Physical Chemistry of the Polish Academy of Sciences (IPC PAS) and the Faculty of Physics of the Warsaw University (FPWU) work has started on the construction of an innovative laser. The compact device will make use of a unique light amplification technology to allow single laser pulses to reach the power of tens of terawatts with world record-breaking amplification parameters.

Most lasers amplify light by making use of classical technology with titanium ions doped sapphire crystals. An external laser is used to pump energy into the crystal where a part of the energy is subsequently taken over by a laser beam being amplified. Laser crystals have, however, numerous disadvantages, e.g., they warm up strongly and distort the cross section of the laser beam. An alternative is provided by parametric amplifiers that exploit non-linear optical effects.

“Our goal is simple. We want to construct the most efficient and compact parametric amplifier in the world”, says Dr Yuriy Stepanenko (IPC PAS).

The multi-pass optical parametric amplifier technology NOPCPA (Noncollinear Optical Parametric Chirped Pulse Amplifier) has been for several years developed in the Laser Centre in a group headed by Prof. Czesław Radzewicz (IPC PAS, FPWU). The method consists in an efficient energy transfer directly from the pumping laser beam to the beam being amplified.

Combined with numerical modelling, theoretical tools developed by our researchers allow to optimize precisely the parameters of both beams and of the amplifier. These issues are non-trivial as field intensity distributions are inhomogeneous in time and space, and in addition the pulse being amplified has a time-dependent frequency (which the physicists call a chirp).

As no energy is being accumulated in a parametric amplifier, there are no damaging thermal effects, and the amplified pulses have excellent parameters. A NOPCPA amplifier has also compact dimensions: a length of several centimetres is enough to reach an amplification of hundreds of millions of times. Theoretical efficiency of such an amplifier is approximately 60% but it is difficult to get, and so far the best laser amplifier of this type reach below 30%.

“Our minimum plan is to reach an efficiency of 40%, we will try, however, to overcome a barrier of 50%”, says Dr Paweł Wnuk (IPC PAS).

The researchers expect to get the first 10 terawatt pulses with duration of dozen femtoseconds emitted by their laser next year. But this is only the beginning of the way. “We hope that already the present version of the parametric amplifier will allow us to generate over 100 TW pulses”, stresses Prof. Radzewicz.

The calculations indicate that 500 TW laser pulses could be used to accelerate protons to energies enabling them to be applied in medical therapies including anti-cancer treatment. The lasers with so high power can be found today only in a few research centres worldwide.

“We have all the grounds to assume that our method of light amplification can in future help us to build relatively cheap lasers for proton acceleration, in addition with so compact size that they essentially would be considered portable devices”, says Dr Stepanenko.

Under the research project being completed the new laser will be used to construct two demonstration setups. The first one, being developed in collaboration with the Military Academy of Technology (MAT) in Warsaw and the Institute of Physics of the PAS, will be used to construct x-ray sources with micrometric dimensions. Such sources are used in, e.g., x-ray microscopy, and in particular in non-destructive testing of structural materials. The second demonstrator will be a lidar for measurements of atmospheric pollution and will be developed with participation of the researchers from the Military Academy of Technology.

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NEW CATALYST AND REVOLUTIONARY FUEL CELLS

You can hardly find a consumer electronics user who would not be irritated by problems with power supply. The batteries are always out, require continuous replacements or a long-lasting charging. Fuel cells could significantly improve the comfort of using electronic devices. Their commercialization, however, is hampered by many technological problems.

A new catalyst, developed at our Institute, represents a substantial milestone on the way to dissemination of cheap, durable, light and environment friendly fuel cells powered by formic acid. Such kind of fuel cells can revolutionize the portable electronics market.

Fuel cell is a device converting chemical energy into electric power. The current is generated directly due to fuel combustion in the presence of catalysts used on the anode and the cathode of the fuel cell.

"Theoretical efficiency of conversion of chemical energy into electric power in the cells can reach even one hundred percent. The best present fuel cells, powered by hydrogen, reach up to 60% in real life. For comparison, the efficiency of low-compression engines is as low as 20%", says Assoc. Prof. Andrzej Borodziński.

The biggest obstacle to dissemination of hydrogen fuels is the storage of hydrogen. The issue turned out to be extremely technologically challenging and still is waiting for satisfactory solutions. A competition for fuel cells powered by pure hydrogen is the methanol fuel cell technology. Methanol, however, is toxic and the methanol powered fuel cells must be produced with expensive platinum based catalysts. Moreover, methanol fuel cells have low power and are operated at a relatively high and so potentially hazardous temperature (approximately 90°C).

An alternative solution are formic acid fuel cells. Here, the reactions occur at room temperature, and the efficiency and power of these fuel cells are clearly higher than those for methanol ones. In addition, formic acid is easy to store and transport. To have, however, formic acid fuel cell stable in operation you need an efficient and durable catalyst.

"The catalyst developed by us has initially lower activity then the existing catalysts made of pure palladium. The difference disappears, however, already after two hours of operation. And further it is only better. Our catalyst is stable in operation, whereas the activity of a pure palladium-based catalyst decreases in time", says Assoc. Prof. Borodziński.

An advantage of the catalyst developed in our Institute, particularly important from the economic point of view, is that it preserves its properties while operated in formic acid of low purity. Such formic acid can be easily produced in large quantities, also from biomass, so the fuel for new fuel cells would be very cheap.

Formic acid produced from biomass would be a fully environment friendly fuel. The reactions involving formic acid in fuel cells generate as products water and carbon dioxide. The latter is, as a matter of fact, a greenhouse gas, but the biomass is obtained from plants which use carbon dioxide for their growth. As a result, formic acid produced from biomass and consumed in fuel cells would not change the content of carbon dioxide in atmospheric air. The risk of natural environment contamination by formic acid is also low.

Formic acid fuel cells would find numerous applications. They would be particularly suitable in portable electronic devices – mobile phones, laptops or GPS-based devices. They could also be installed as power supply sources in vehicles, from wheelchairs through electric bicycles up to yachts.

At the IPC PAS the research is being undertaken on the first batteries based on formic acid fuel cells. Our researchers expect that a prototype of a commercial device should be ready within a couple of years.

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...TO ORGANISE!

It’s not enough to understand, to see and to make use. Modern science must be alive – conditions must be provided to allow for a stable existence and development of science in a way as to bring measurable benefits for the society and to encourage young people to tackle ambitious intellectual challenges.
THE FIRST INSTITUTE OF THE PAS TO ENTER A SPIN-OFF COMPANY

Because of legal barriers, until the end of 2010, the institutes of the Polish Academy of Sciences were not allowed to set up companies to commercialize their own inventions. These limitations represented substantial hindrance to the transfer of scientific inventions to the industry and gaining additional funding for the research institutions.

Present legal regulations have allowed our Institute to take up shares in Scope Fluidics, a young spin-off company pursuing scientific research, developing innovative technologies and designing microfluidic devices for medical and biotechnological applications. The purchase of shares in the company was possible due to the last year’s amendment to the Act on the Institutes of the Polish Academy of Sciences. The amendment to the Act took place in October last year. A few weeks later our Institute obtained the permission from the Ministry of Science and Higher Education and could officially take up 10% shares in Scope Fluidics.

“In the course of research work you can make a discovery, but you can not implement it into practice. The implementations require simply a plenty of work that can not be scientifically substantiated”, says Assoc. Prof. Piotr Garstecki, the research director and president of Scope Fluidics.

Prof. Hołyst, the managing director of the IPC PAS, emphasises that it is the role of a research institute to provide support to small companies trying to transfer scientific ideas to the industry.

“In these activities we must keep within the limits of the common sense. We are interested in securing some future revenues from implementation of our inventions, but we do not want to manage the company. We are doing science, not business. That’s why ten percent is an adequate share”, said Prof. Hołyst.

Scope Fluidics is a young dynamic spin-off company operating in the IPC PAS campus. During one year of activity the number of company’s employees increased from one to nine. The company has just completed a few months long initial research program for an European industrial partner. They managed to successfully demonstrate that certain academic discoveries can be implemented in an industrial scale.

“Now the company starts to perform a large contract for construction of prototype microfluidic systems”, stresses Marcin Izydorzak, the managing director of Scope Fluidics.

Prof. Hołyst sums up the taking up of shares in the first spin-off company by the Institute of Physical Chemistry of the PAS: “We managed to get to the point, where sound rules of cooperation make it possible to translate effectively scientific discoveries into industrial innovations. Rapid development of Scope Fluidics proves that it is a promising way. The most important is, however, that now we have an open way to effective cooperation with the industry”.

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GREEN CHEMISTRY MAKES ITSELF AT HOME IN MAZOVIA

A Mazovian Valley of Green Chemistry is emerging – a strong research infrastructure aggregating the best chemistry-related institutions from Warsaw and the area around Warsaw. The main Valley’s objective is to develop a friendly environment, conducive to dynamic development of various fields of chemistry and to fast transfer of research findings to the industry.

Over a dozen chemistry-related research institutions from Warsaw and Mazovia, including research institutes, institutes of the Polish Academy of Sciences (PAS) and universities are joining efforts in the framework of a distributed knowledge and technology transfer incubator named Mazovian Valley of Green Chemistry. Unique in Poland, the project has been already proposed to be included in the Polish Road Map for Research Infrastructures comprising scientific initiatives with the highest priority for the state’s development. The project was presented to Adam Struzik, the Marshal of the Mazovian Voivodship, and gained his support.

“The Mazovian Valley of Green Chemistry is a response to the initiatives of the Ministry of Science and Higher Education with regard to establishing the Polish Road Map for Research Infrastructures that is short of projects from chemistry, chemical engineering and material sciences. This is also a response to Marshal Struzik’s appeal for proposals to enrich the Development Strategy for the Mazovian Voivodship. The Valley will provide friendly environment for intensifying cooperation in developing innovations and innovativeness, and for increasing internationalisation of companies in the voivodship, thus contributing to a stimulation of Warsaw’s metropolitan development as well. It is one of a very few projects to join efforts and activities of universities, institutes of the Polish Academy of Sciences and research institutes”, says Prof. Andrzej Chmielewski, the director of the Institute of Nuclear Chemistry and Technology, who spoke on behalf of the research institutes in the meeting with Marshal Struzik.

The PAS institutes were represented by Prof. Robert Holyst, the director of the Institute of Physical Chemistry of the PAS, and the community of Mazovian higher education institutions was represented by Prof. Eugeniusz Molga and Prof. Jerzy Szawłowski from the Warsaw University of Technology.

The Mazovian Valley of Green Chemistry was initiated by Warsaw’s chemical community during the celebrations of the International Year of Chemistry in June 2011. At present, the following institutions are involved in the project: Warsaw University of Technology – the School of Advanced Chemical and Material Technologies, Warsaw University – the Faculty of Chemistry, Military University of Technology – the Faculty of New Technologies and Chemistry, the Institute of Physical Chemistry of the Polish Academy of Sciences, the Institute of Organic Chemistry of the Polish Academy of Sciences, the Institute of Nuclear Chemistry and Technology, the Industrial Chemistry Research Institute, the Pharmaceutical Research Institute and the Institute of Industrial Organic Chemistry.

According to the initiators’ intention, the Mazovian Valley of Green Chemistry is going to be a strong research structure, exploiting the research potential of the research institutes, the PAS institutes and the chemical faculties of higher education institutions and cooperating with engineering design offices and the industry. The access to well-equipped laboratories and semi-technical pilot plants operated within the Valley will also contribute to the development of various areas of chemistry. The Valley will also provide support for educational and information programmes from chemistry and related sciences, including scientific conferences, doctoral studies, postgraduate studies and scientific visits for foreign students as well as public presentation of scientific achievements.

Since the middle of 2011, the Mazovian Voivodship is a member of the European Chemical Regions Network, ECRN. At present, the network consists of 21 European Regions, where the chemical industry plays an important role. The emerging Valley will therefore naturally contribute to an increasing Mazovia’s importance on the chemical map of Europe.

The most important objectives of the Mazovian Valley of Green Chemistry include encouraging young researchers to establish companies to transfer innovative chemical technologies to the industry and the market.
“We all are vitally interested that the graduates, and even students, can establish spinoff companies. These companies guarantee the transfer of knowledge to the industry and offer jobs to creative people. By-and-by, after reaching a critical mass, one of them will grow to a global concern that will provide support to Polish science, which is still underfinanced as compared with other European competitors. It was the case in Finland and we want to achieve the same in Mazovia”, says Prof. Hołyst.

In the Valley, young spinoffs can be provided with legal assistance in securing venture capital funding, and their representatives will be aware where to look for innovative ideas.

One of the first activities towards establishing the Mazovian Valley of Green Chemistry is the E-Lab data base of accessible laboratory equipment. The E-Lab data base is shared by interested parties and is being developed within a NO-BLESSE project carried out by our Institute. It is planned that in the next step a data base with scientific specialisations will be developed. The access to both data bases will largely facilitate the start-up for young spinoff companies who must often use sophisticated research equipment and consultation with top-class experts in the initial phase of their business activity.

The initiators of the project emphasise that the present stage of development of the Mazovian Valley of Green Chemistry does not require any additional sources for its funding. At future stages, high scientific level of institutions participating at the consortium and the cooperation with the industry should provide revenues to guarantee efficient project functioning.

Micro- and nanodroplets flowing inside barely visible channels may serve as miniature chemical reactors. The research in this modern area of contemporary chemistry can be pursued more effectively with our Ultrafast Microfluidic Devices Laboratory that has been opened on 6th March, 2012.

The opening ceremony was attended by the representatives of over a dozen of Poland’s largest scientific institutions – members of the NanoBioGeo consortium.

Microfluidic systems transport carrier fluids with microdroplets containing chemicals through appropriately designed, easy to construct and cheap to fabricate channel systems. A comprehensive understanding of phenomena occurring in microflows as well as the development of technologies for manufacturing, transporting, merging and partitioning microdroplets of various chemicals is of crucial importance for the development of the field.

“Our new laboratory provides a platform for research into phenomena in microfluidic systems. The main objective is to observe and record optically ultrafast transport processes at the microscale and nanoscale, such as flows or diffusion”, says Assoc. Prof. Piotr Garstecki.

The state-of-the-art Laboratory’s equipment allows for employing many microscopic techniques, including fluores-
cience and bright field microscopies. The equipment allows us also to conduct studies in the area of fluorescence correlation spectroscopy.

Microfluidics is a promising and expanding area of research. Many scientists agree that microfluidic systems will change the face of contemporary chemistry to a comparable extent as the integrated circuits have changed electronics in 1970s.

The newly opened laboratory is operated within the Department of Physical Chemistry of Soft Condensed Matter and Fluids of our Institute. It is another one launched from among fourteen laboratories arising under the project National Multidisciplinary Laboratory of Functional Materials – NanoFun. The project is implemented by the NanoBioGeo consortium under the Innovative Economy Operational Programme 2007-2013.

The equipment of the Ultrafast Microfluidic Devices Laboratory can be accessed by the institutional members of the NanoFun consortium and by external users, both domestic and international. More information on the Laboratory can be found at:

http://pepe.ichf.edu.pl/nanofun/

The NanoFun’s main objective is to establish a network of over a dozen laboratories pursuing innovative inter- and multidisciplinary research with potential applications in nanomaterials, biochemistry, biophysics and chemical engineering.

The research infrastructure emerging in Poland under the NanoFun project will be used by more than 100 research institutions and companies, and about one thousand of students. It is expected that the infrastructure will allow to complete about 150 international research and R&D projects, with participation of a few hundreds of researchers from various international organisations including Harvard University, University of California, Johns Hopkins University, University of Toronto, McGill University, London University, Centro Nacional de Biotecnologia, Max Planck Institute, Ecole Politechnique and Queensland University of Technology.

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© Felice Frankel lecturing at our Institute. (Source: IPC PAS, Grzegorz Krzyżewski)

FELICE FRANKEL ABOUT SCIENCE PHOTOGRAPHY

Their uniqueness immediately attracts attention. They fascinate by beauty, intrigue by form. In the photographs taken by Felice Frankel science is presented in an uncommon, often surprising way. Frankel, a world-famous science photographer, talked about her experience and methods of work in our Institute in April 2012, during an open lecture and an all-day workshop for scientists.

Felice Frankel’s photographs are not dry documents from the laboratory work. In balanced proportions they combine scientific message with well thought-out visual aesthetics. The play of light underlines the perfection of shape of a droplet trickling down from a pipette. The eye is catch by the spirals of chemical fronts in Belousov-Zhabotinsky reactions. The cones of a ferrofluid stand upright in a carefully shaped magnetic field. The canvas used by Frankel are the phenomena of Nature, and the brush – the tools of science.

“I am often called an artist. But I am not. An artist expresses himself or herself. For me the ultimate goal is to express science”, says Felice Frankel.

Before devoting to imaging the scientific accomplishments, Frankel was a researcher in the Cancer Research Institute at the Columbia University. Her own research experience provided an excellent basis for working with other researchers on imaging their accomplishments. The photographs taken by Frankel not only landed on the covers of the
most prestigious scientific journals such as “Science”, but could also be frequently found in the popular press or were presented in an open-air exhibition in Elysian Fields in Paris.

At present Frankel works in the Center for Materials Science and Engineering at the Massachusetts Institute of Technology. Her interests include not only photography but also other methods for graphical representation of science and its findings.

“Photographs, illustrations and diagrams are visual language that is perfectly understood by all recipients, and that makes science more accessible. People are not afraid of images, they are not afraid to ask questions about what they see. And that’s what I want: that looking at my photographs people start to ask questions”, explains Frankel.

Sophisticated visual form of Frankel’s images encourages to ask questions. The answers are provided by text, obligatorily attached to each photograph.

“In the picture I can show, for instance, a beautiful bubble that presumably will be liked by many spectators. But it is not only the beauty that matters here. The most important thing is that the recipient notices science hidden behind the image. That’s why the explanatory text is necessary, as the image only does not produce the intended effect”, stresses Frankel.

**GOLDEN MEDAL OF CHEMISTRY**

The special final of the first edition of the Golden Medal of Chemistry competition was held in late 2011. The competition, organised on our Institute’s initiative and supported by the Foundation for Polish Science, attracted a few dozens of authors of bachelor or bachelor of engineering theses in chemistry and related sciences from all over the country. The main prize was awarded to Marcin Runowski from the Faculty of Chemistry, Adam Mickiewicz University in Poznań. The prize winner received the Golden Medal of Chemistry from Prof. Maciej Żylicz, the President of the Foundation for Polish Science.

“The level of theses and presentations delivered by the finalists was very high. They are barely bachelors, and even so many have authored their own scientific publications, some even patent applications. Admittedly, I happened to review doctoral dissertations with poorer scientific record”, says Prof. Robert Hołyst, the director of the IPC PAS.

From among the theses submitted for competition, the competition committee selected 15 finalists, who were awarded four distinctions and three prizes. The main prize – the Golden Medal of Chemistry and 10,000 PLN – received Marcin Runowski from the Faculty of Chemistry, Adam Mickiewicz University in Poznań for the thesis “Synthesis and photophysical characterisation of lanthanide ions doped hybrid luminophores based on core/shell structures”. The second prize – the Silver Medal and 5,000 PLN – was awarded to Robert Lasek from the Faculty of Biology, Warsaw University. The third prize – the Bronze Medal and 2,500 PLN – went to Celina Wierzbicka from the Faculty of Chemistry, Wrocław University of Technology.

Equivalent distinctions and financial prizes of 1,000 PLN each received: Jędrzej Marciniak from Adam Mickiewicz University in Poznań, Krzysztof Sozański from Warsaw University, Małgorzata Wolska from Warsaw University of Technology and Karolina Żukowska from Warsaw University. The finalists of the competition awarded their prize to Marcin Runowski.

“Research topics addressed by the prize winners, such as nanomaterials, synthesis of biologically active chemicals or industrial catalysis, fit remarkably research trends of modern chemistry”, emphasises Prof. Andrzej Kapturkiewicz, the coordinator of the competition.

Magnetic nanoluminophores are light emitting chemicals forming structures of nanometer sizes. Their characteristic property is their capability to respond to magnetic field. “Such nanoparticles have been studied worldwide for a few years only and stimulate growing interest”, says Marcin Runowski.
the Golden Medal winner. “It turns out that after appropriate modification, they can be surrounded with a protection shell. Then they become nontoxic and can be introduced into patient’s body, for instance, to perform fluorescence imaging. It is of paramount importance that they can be removed from the body using magnetic field”.

Robert Lasek, the second prize winner, works with a strain of cryophilic bacteria isolated by the personnel of the Polish research station in Spitsbergen. The research is bioinformatics-oriented and consists in computer-assisted analysis of the genetic code of bacteria. “Little is known on the biology and genetics of bacteria living at low temperatures. But at the same time, understanding of chemical processes occurring in these organisms can be of measureable importance, not only for science”, says Lasek. “After all, cryophilic bacteria produce enzymes which decompose fats and carbohydrates at low temperatures – that is they do the same we would expect from really good washing powders”, he explains.

Celina Wierzbicka received the third prize for her bachelor of engineering thesis on catalysts used in the metathesis of olefins, completed in Apeiron Synthesis, a spin-off company from the Wrocław Technological Park. “The metathesis reaction consists in exchanging carbon atoms between a pair of double bonds in a molecule. I studied catalysts of these reactions, synthesised using ruthenium”, describes Wierzbicka. “The subject matter of the thesis was to analyse the effectiveness and stability of two catalysts having groups with different structures – ligands – attached to the ruthenium atom”. The research is important for the industry as the new catalysts can improve the metathesis of olefins, a reaction used, i.a., in the synthesis of drugs, polymers, cosmetics and pesticides.

All the finalists have been also offered research internships in our Institute and an opportunity to perform research in the Institute’s laboratories free of charge. Such a research can then become a basis for a master thesis or doctoral dissertation. In particular cases, for students from outside Warsaw, the Institute provided support for the accommodation costs for the period of collaboration.

In June 2011, our Institute together with the Institute of Organic Chemistry of the PAS organised the celebration of the International Year of Chemistry 2011, with the honorary patronage taken by the President of the Republic of Poland, Bronisław Komorowski.

The purpose of the International Year of Chemistry 2011, established by the United Nations, was to draw public attention to the contribution of chemistry to the development of humanity and the key role of this field of science in functioning of contemporary societies. The aim of the celebration was also to highlight the importance of chemistry in solving global challenges of civilization, increase interest of youth in chemical matters and stimulation of cooperation between scientific and research institutions. In Poland, the International Year of Chemistry 2011 coincided with the Year of Maria Curie-Skłodowska, proclaimed by Polish Parliament.

The first closed-door day of the event was scheduled for meetings of the representatives of academia with those of the industry. “We showed our guests, how much potential lies in the Polish chemistry”, says Prof. Robert Holyst, the director of our Institute. The second day of the event was open for all interested. The organisers opened their exhibition tents for the public. The pupils from primary schools were offered to take part in a “Chemical Harry Potter” Magic Tournament that was prepared with common efforts of the organisers.
It was a sort of a location-based game, where teams of three persons competed for a cup. To win the cup, one had to learn nuances of preparation of various elixirs, to trace instructions distributed in the exhibition area and to solve chemical riddles. Junior high school students and high school students could prove themselves in individual competitions, and afterwards take part in interesting lectures on chemistry.

The celebration involved shows of particularly interesting experiments that could be safely performed by professionally trained chemists only because of reagents or the nature of reactions. Our Institute showed, i.a., exploding volcanoes, “magic” colour-changing fluids, squirming pharaoh’s snakes and chemical gardens with multicoloured “plants” growing in eyes. Courageous participants of the event could taste a light emitting drink in a dark room. “This are only some of the attractions prepared by our Institute. Besides us, the event was co-organised by over a dozen chemical organisations, each presenting their own show programme”, stresses Dr Roman Luboradzki.

The following institutions were among the organisers of the International Year of Chemistry: the Institute of Organic Chemistry of the PAS, the Committee of Chemistry of the PAS, the Faculty of Chemistry, Warsaw University, the Institute of Nuclear Chemistry and Technology, the Faculty of Chemistry, Warsaw University of Technology, the Institute of Physical Chemistry of the PAS, the Faculty of New Technologies and Chemistry, Military Academy of Technology, the Faculty of Mathematics and Natural Sciences – College of Sciences, Cardinal Stefan Wyszyński University, the Institute of Catalysis and Surface Chemistry of the PAS, the Industrial Chemistry Research Institute, the Faculty of Materials Science and Engineering, Warsaw University of Technology, the Pharmaceutical Research Institute and the Faculty of Chemical and Process Engineering, Warsaw University of Technology.

Media patronage over the celebration was taken by TV Biznes, the First Programme of the Polish Radio, Onet.pl web portal and editorial offices of the “Wiedza i Życie” and “Świat Nauki” monthlies. Among the sponsors were the companies: LOTOS S.A., PRECOPTIC sp. z o.o./NICON, PREVAC sp. z o.o., CORMAY S.A., ALAB sp. z o.o. and Warsaw Trams Corporation (Tramwaje Warszawskie).
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