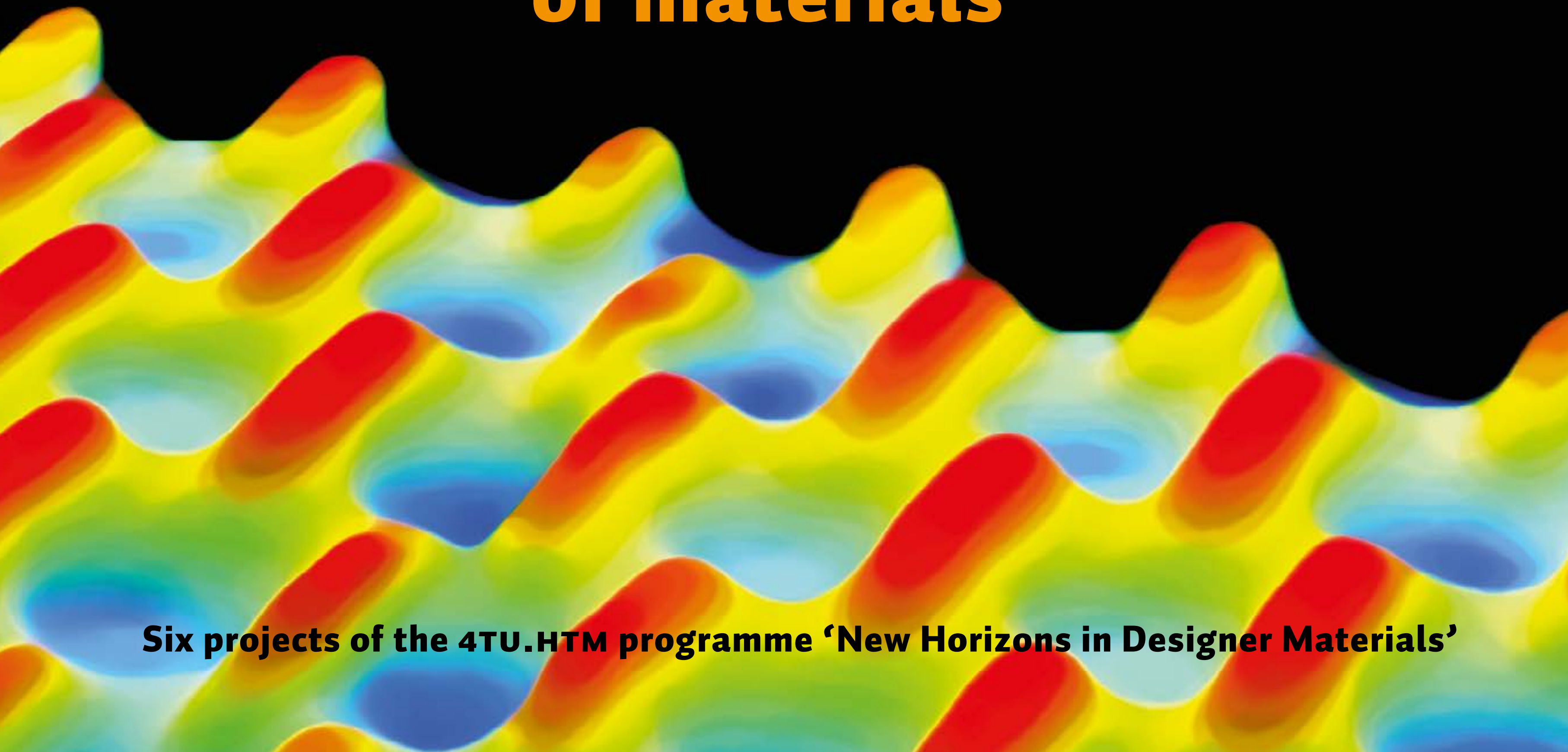
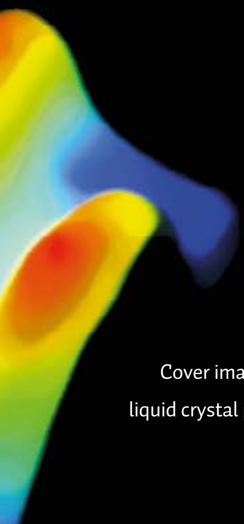
Stretching the boundaries of materials



Six projects of the 4TU.HTM programme 'New Horizons in Designer Materials'



Cover image: Graphic designer's impression of 'Surface protrusions formed in a liquid crystal polymer network'. [Danqing Liu, Eindhoven University of Technology]

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Six projects of the 4TU.HTM programme New Horizons in Designer Materials

4TU.Research Centre
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Content

The Boundaries of Materials

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Use this code to hear
a reading of this poem

www.samillingworth.com

These are the essential building blocks of life
And non-life
Materials that are imbued
With barely believable features,
Pushing beyond limits that others
Define as traditional.
Following pathways of conservation
And least resistance,
Their dynamic, vibrant features
Slowly begin to emerge:
Stiffening,
Softening,
Healing,
Radiating light,
Resisting translucency.

These are the molecular manipulations that we

Must strain to stimulate,

Embracing entropy with every unformed idea,

Every swirl of caffeine,

Every shattered dream.

***W**e race to create an elixir of life;*

Designer macromolecules

That extend their existence

Beyond the blink of an eye,

Radically tricking their termination

To bind their ions and bend their chains.

And yet,

***A**s we enter into the second century of our co-existence*

We are still to reach the sophistication of nature;

A macromolecular nirvana where

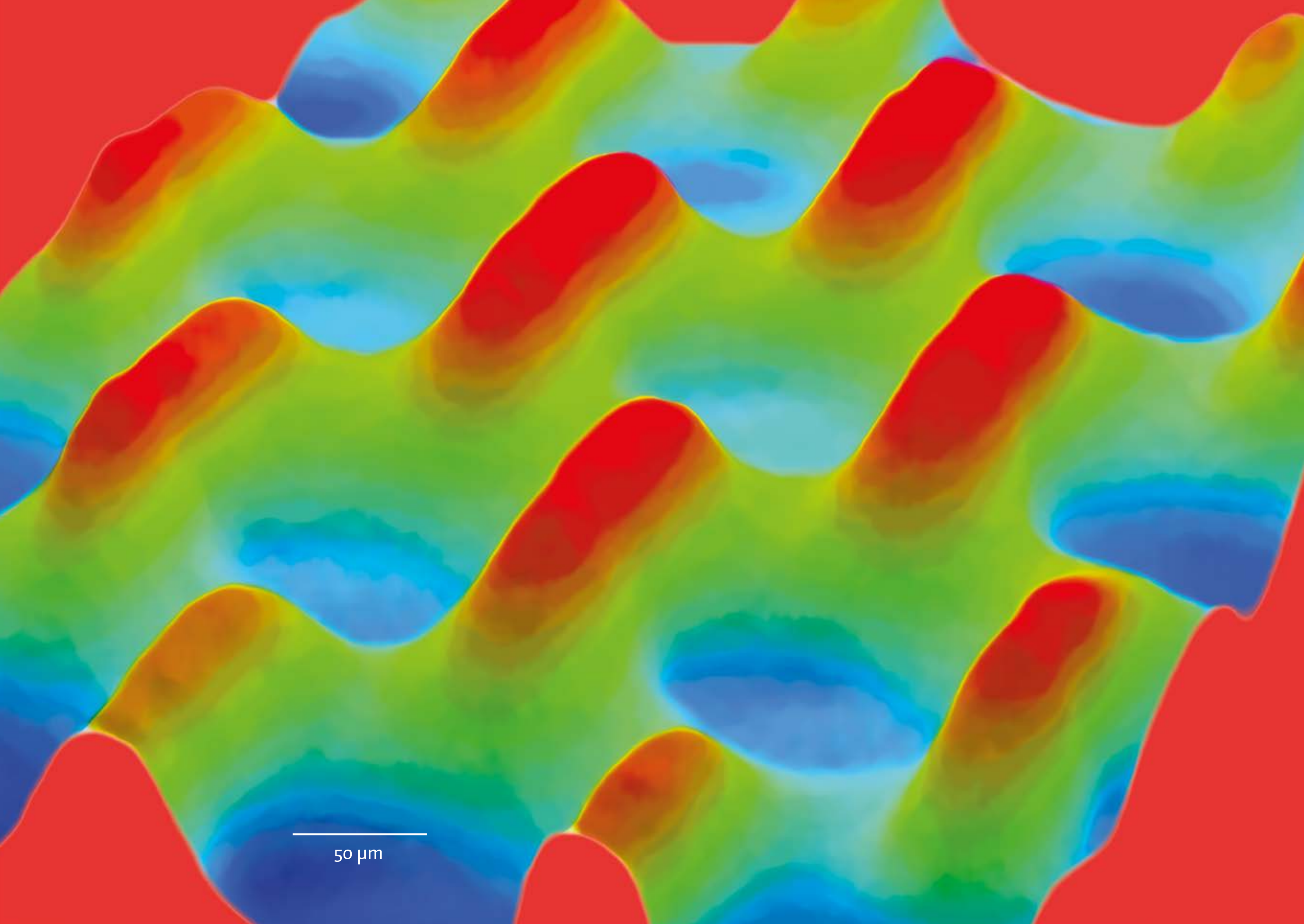
Environmentally friendly, oxygen-tolerant,

And easier to use materials cast off the

Diabolical characteristics of their surfaces,

To finally embrace their borders

With our external world.


50 µm

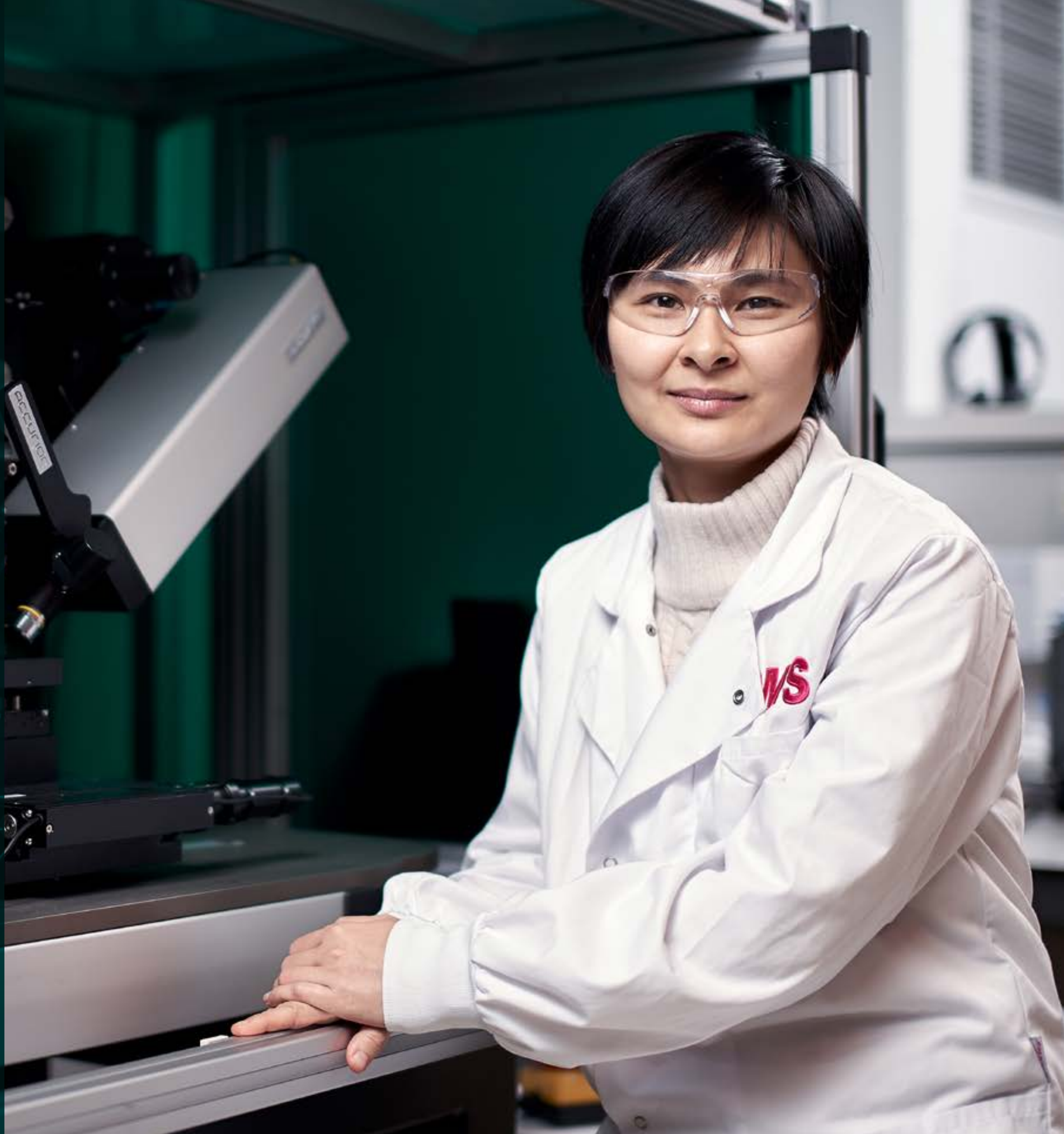
Project title: Communicating Surfaces
Postdoc: Dr. Danqing Liu
Supervisor: Prof. Dirk J. Broer
University: Eindhoven University of Technology
International expert: Prof. Peter Palffy-Muhoray (Kent State University, USA)

Can robots get goose bumps?

"Surfaces are the interface between man and material," Dr. Danqing Liu writes in the prestigious journal *Nature Communications*. They therefore play a crucial role in the exchange of information between the two. While we are used to endlessly watching and listening to our smartphones, computers and televisions, these devices do not appeal much to our sense of touch. Touchscreens feel what our fingers are doing, not the other way around. And that is strange, since touch is a sense that is not to be underestimated. Research from 2013 suggests that our fingers can feel extremely small height differences, down to a nanometre. "We can make materials smarter by making them adapt their surface texture as desired," says Danqing. But how do you make a surface change its texture in a controlled manner so that it can give a human finger something to feel? "Layers of piezoelectric materials, electro-active polymers and hydrogels are well-known to change shape under the influence of an electric field, but only if you place an electrode under and on top of them and apply a large voltage of up to 1000 V. They are therefore not very practical as layers to be touched and felt." The objective of the 4TU.HTM project 'Communicating Surfaces' was to develop a polymer surface that safely and in a controlled way converts electrical signals into touchable surface patterns.

Postdoc: **Dr. Danqing Liu**

Dr. Danqing Liu studied electrical engineering at Delft University of Technology. Keen to explore a different field, she moved to mechanical engineering, which is where she became interested in materials. She obtained her Ph.D. in the field of responsive polymers at Eindhoven University of Technology. During her postdoc project at the Department of Chemical Engineering and Chemistry, she wrote the 4TU.HTM proposal. "HTM stands for high-tech materials, and that term describes exactly what I am working on." Her work on the project resulted in a string of publications in journals such as *Nature Communications*. This success and Danqing's ideas were rewarded with a Veni grant from the Netherlands Organisation for Scientific Research (NWO). In 2015 Danqing was a Research Fellow at the Institute of Complex Molecular Systems in Eindhoven. From 2019 she is appointed as Assistant Professor (Tenure) at the Department of Chemical Engineering and Chemistry, Eindhoven University of Technology.



“We had the Mars Rover in mind, the famous space vehicle.”

Ripples in plastic To cut a long story short, Danqing and her team succeeded with flying colours. “We created a thin electrode structure underneath a layer of liquid crystals trapped in a polymer network. The electrodes have an interdigitated structure, like interlocking fingers separated by about 10 micrometres. If we apply a voltage of 70 V, an electric field in the plane of the polymer layer is generated that is strong enough to force the liquid crystals in the polymer network out of their preferred arrangement.” This arrangement is preferred because it has the molecular structure that takes up the least volume. If the molecules are forced to arrange themselves differently, the volume of the layer increases. In other words: a thin corrugation or ripple is created in the plastic layer where the electric field is applied, which disappears when the voltage is removed. “This was an important breakthrough for us. Integrating electrodes underneath the polymer layer was a completely new approach. It was also the first time that this type of organic material was actuated by an electric field.” Danqing is poised to bring the voltage down even further by turning to softer polymer networks that make it easier for the liquid crystals to move when an electric field is applied.

Shaking off extra-terrestrial dust It is not just electric fields actuating the coatings. Other possible triggers are temperature, light, acidity or environmental changes. The potential applications are manifold and Danqing has no shortage of appealing examples. Visions of programmable braille, tactile keys on touch screens and self-cleaning surfaces found their way to the national and international news. For example, in a particularly convincing video clip, Danqing demonstrates that a thin, transparent polymer layer can shake off an amount of sand with the help of a single voltage pulse. “In developing this proof of principle, we had the Mars Rover in mind, the famous space vehicle.” Mars is home to planet-wide dust storms. If this dust covers the Rover’s solar panels, it will lose power and eventually stop functioning. Danqing’s polymer layers could help keep those panels free of sand. NASA has already contacted the scientists. “This project

"This technique could help machines communicate with each other through a very human type of interaction: physical contact."

was a direct spin-off from the innovation that we developed in the 4TU.HTM project."

Hard and soft robots But Danqing is mainly interested in the use of the responsive layers to facilitate communication between man and machine or between machines. Robots now consist mainly of hard materials that do not invite being touched. The alternative technical development of soft robotics has the disadvantage that it, precisely because of its softness, can exert small forces only, for example to pick up or move an object. The communicating polymer layers developed by Danqing can become an attractive interface between man and machine. "The topography of the surface contains information that can be passed on. Think for example of virtual reality, not only for entertainment purposes but also for surgeons to practice delicate procedures. Virtual reality now only gives them visual cues to base their movements on. What if they can also feel something when they almost puncture the training tissue and therefore have to be extra careful? Haptic feedback is an important development to help surgeons operate more safely and accurately," says Danqing. This technique could also help two machines to communicate with each other through a very human type of interaction: physical contact. "A robot will be able to feel the surface topography offered by another robot, like scanning a finger print or sensing goose bumps."

Firm grip In another proof of principle in the field of robotics, Danqing showed that the electrically controlled surface topography can also be used to finetune the surface friction. "Imagine a robot holding something fragile," Danqing explains. "We need ways to finely tune the robot's grip and to allow it to release the object in a controlled fashion. The materials used for soft robotics are often sticky, making the release something of a challenge. Surface friction could mean the difference between abruptly dropping the object and letting it go gently."
By actuating a polymer surface to go from flat to a fingerprint-like pattern of corrugations of less than a micrometre in height, Danqing showed that the effective contact area between robot and object decreases, resulting in lower

friction and therefore in the smallest possible easing of the robot's grip.

Sweaty polymer layers The most recent development that resulted from the 4TU.HTM project also attracted a lot of attention. For this, Danqing went from polymer layers that change the volume on demand to polymer layers that absorb or release a quantity of liquid when triggered. "We use the same principles to get thin sponge-like layers, filled with liquid, to squeeze themselves and release the liquid. This can be a local effect, activated by an optical or electrical signal." Why do you want a polymer layer to sweat? "These layers can be used to apply a liquid locally and in a controlled manner, for example some type of medicine, a lubricant or a dirt-repellent coating. The great thing about our polymer layers is that they can be refilled over and over, if needed with different liquids."

Commercial products Looking back at the string of publications and proofs of principle realised, it is clear the 4TU.HTM project was a success. "We were very well →

New opportunities for familiar crystals

The materials that Danqing successfully set in motion are based on liquid crystals, a type of material that is mainly known as the magical ingredient of thin liquid crystal displays (LCDs). As the name suggests, the molecules form crystal-like structures. The rod-shaped molecules are arranged in a spiral structure in which each molecule is slightly rotated relative to its neighbour. This arrangement causes the polarisation direction of the light passing through the crystals to change. But where a traditional crystal is stuck in a certain ordering, the liquid variants are easier to deform. For example, the arrangement of the molecules and thus the polarisation direction of the light can be changed by exposing them to an electrical voltage. This property forms the basis of the LCDs: electrical signals determine the optical properties of the display material.

Danqing uses a similar principle, but with the tactile properties of the layer. "Producers of chemicals such as Merck find that the liquid crystals in displays are slowly but surely being replaced for example by quantum dots or OLEDs. So, they are looking for new applications of the old materials."

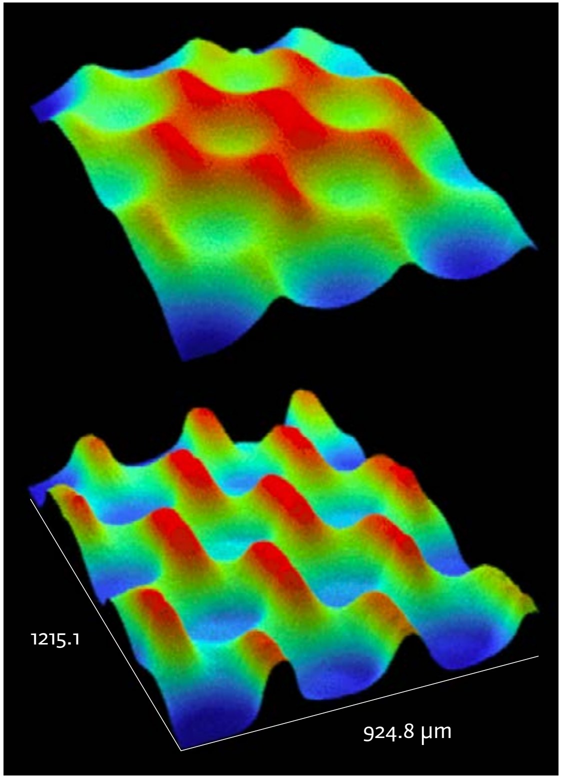
The silent force behind this effort is Prof. Dirk J. Broer, Eindhoven University of Technology's long-time liquid crystal expert. Thirty years ago, he started working on liquid crystals embedded in polymer networks. The polymer network provides flexible crosslinks between the crystals, which ensure that the material returns to its original configuration after a deformation under the influence of, for example, an electrical voltage. It is this type of material that forms the basis for the 4TU.HTM project.

"How do we translate molecular functions to functional materials?"

prepared, and lucky," explains Danqing. She hopes that within 10 years her materials will be used in technology that we use every day. Isn't that very fast? Danqing emphasises that she wants to focus primarily on pioneering new concepts and the scientific aspects thereof. Nonetheless, behind the scenes, the heat is on to scale up the processes. Together with international chemicals manufacturer Merck, the team patented their findings, and in collaboration with South China Normal University they established an institute to demonstrate the feasibility of commercial products. In 2015, Prime Minister Mark Rutte opened this Laboratory for Device Integrated Responsive Materials (DIRM) in Guanghzou. Prototypes are made here based on the ideas from Eindhoven University of Technology. The programmable ripples are not yet in production as the team wanted to start with a simpler system: glass panels covered with liquid crystals that go from transparent to opaque at the touch of a button.

Knowledge gap Reflecting on the field of designer materials, the topic of the 4TU.HTM funding programme, Danqing stresses a particular challenge: "How do we translate molecular functions to functional materials? Only a few people have that expertise. A single molecule can have a fancy functionality but this is not easily translated into the collective behaviour of many such molecules in a material. I think there is a huge knowledge gap. Perhaps future funding programmes could address this gap and stimulate synergy between molecular chemistry and materials science." Danqing and colleagues are committed to closing the gap between disciplines, and currently developing a new course in this area. "We really want to make students aware," she concludes. Students can learn from the Eindhoven team indeed: supported by the 4TU.HTM programme, Danqing has successfully covered the *entire* development chain, from molecule to material, and even a step further to a proper device, ready to be turned into a viable technology.

Surface protrusions emerging in a thermally responsive liquid crystal polymer network when the temperature is raised (from top to bottom picture).



International expert:

Prof. Peter Palffy-Muhoray

Prof. Peter Palffy-Muhoray is Professor of Chemical Physics at Kent State University (USA) and an internationally recognised expert in the field of liquid crystals.

"The work in the 4TU.HTM project is part of a larger community effort working on robotics based on soft materials. Although many breakthroughs are needed to realise viable devices, the hope is that the materials, as investigated by Dr. Danqing Liu, will evolve in self-sustaining constructs that can perform pre-set functions by deforming in complex, but pre-designed, manner. One of the topics that I often discussed with the researchers at Eindhoven University of Technology concerns materials that can communicate information by their deformation. The idea is that they can effectively relay the sense of touch over large distances, so that a remote person can feel the touch of another person, for example, which would be of interest in the world of augmented reality."

Liquid crystals through thick and thin

In a parallel project, Dr. Nicholas B. Tito flexed his simulation muscles by looking at a polymer system that is driven out of equilibrium in a different way. "Here it was not the crosslinks that influenced the dynamics of the polymer material, but an external electric field." For this, Nicholas entered into a collaboration with another 4TU.HTM project, that of Dr. Danqing Liu at Eindhoven University of Technology. "She looks at liquid crystals in a polymer network. The liquid crystals are sensitive to electric fields, so if you put an oscillating voltage across the network, the molecules move back and forth, opening up pockets of nanometre-scale empty space. This results in the material as a whole changing in volume. But under what circumstances are these volume changes largest? In experiments, Danqing saw that this was when the temperature was raised to the so-called glass temperature of the polymer, the temperature at which the material becomes very soft. With our simulations we were able to simulate this behaviour: we too found a temperature at which the volume change was maximal. At lower temperatures the polymers do not have enough energy to make room, at higher temperatures they are so mobile that an empty space opened by a mobile liquid crystal is immediately filled up by another, which reduces the net change in volume. A major achievement was that supporting simulations allowed us to estimate the glass temperature, too; the two temperatures found in the simulations were the same. And so, our qualitative approach had turned quantitative!" Now that the simulations had proven themselves, Nicholas and Danqing apply the same approach to other questions. For example, what is the role of the frequency of the electric field?

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