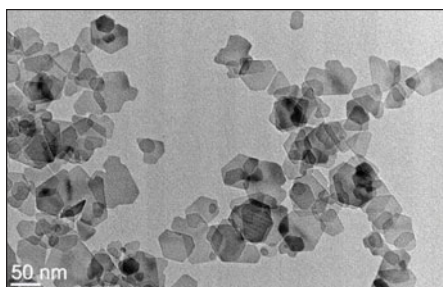


Ferromagnetism revealed in suspensions of magnetic nanoplatelets in liquid crystal

Inspired by their beautiful color patterns viewed in an optical microscope and their intriguing behavior, Alenka Mertelj from the J. Stefan Institute in Ljubljana, Slovenia, developed an interest in the dynamics of complex fluids. Now she and her colleagues at the Insti-



Transmission electron microscope image of magnetic nanoplatelets. Image credit: Alenka Mertelj.

tute—Darja Lisjak, Miha Drofenik, and Martin Čopič—have added a new dimension to that complexity: ferromagnetism.

Previous to their work, ferromagnetic complex fluids had only been observed at either liquid helium temperatures or above 1000 K. By mixing nanoparticles in a nematic liquid crystal, the research team succeeded in making a room-temperature fluid ferromagnetic phase, thereby solving a 40-year-old problem. The issue at hand: avoid aggregation of the nanoparticles while maintaining sufficient magnetic interaction between them. Their trick: the use of magnetic nanoplatelets. As reported in the December 12, 2013 issue of *Nature* (DOI:10.1038/nature12863; p. 237), the researchers found that the platelet shape of barium hexaferrite particles allows for a suitable interplay between the magnetic and nematic-elastic interactions, and combined with quench-cooling of the suspension from the isotropic into the nematic phase, stable, aggregate-free samples are formed.

Proving that the concept works, their samples showed hysteretic magnetization switching at very low magnetic fields. Furthermore, depending on the fabrication procedure employed, mono-domain behavior (for samples cooled in a magnetic field) or multi-domain behavior with domain wall motion was observed.

Adding ferromagnetism to the well-established electro-optical properties of liquid crystals means these materials represent a new class of multiferroics. They may enable many new applications, especially in magneto-optic devices. Mertelj said, “Whereas in liquid crystals one can control the propagation of light by an electric field, this new material may allow similar control by a magnetic field. Or they can be used to image the magnetic field with a liquid crystal.”

The use of other (chiral or smectic order) types of liquid crystals has the potential to further open up a completely new research field.

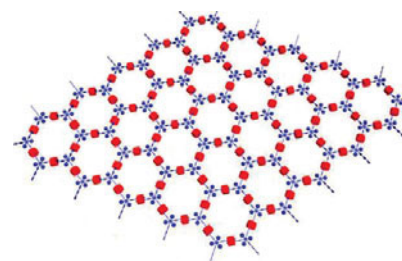
Dirk Wouters

Soluble 2D supramolecular organic frameworks created

Supramolecular chemistry, in which molecules and molecular complexes are held together by noncovalent bonds, is just beginning to come into its own with the emergence of nanotechnology. Metal-organic frameworks (MOFs) are commanding much of the attention because of their appetite for greenhouse gases, but a new player has joined the field—supramolecular organic frameworks (SOFs). Researchers with Lawrence Berkeley National Laboratory (Berkeley Lab) have unveiled the first known two-dimensional (2D) SOFs that self-assemble in solution, an important breakthrough that holds implications for sensing and separation technologies, energy sciences, and, perhaps most importantly, biomimetics. The researchers report their work in the September 30, 2013 online edition of the *Journal of the American Chemical Society* (DOI: 10.1021/ja4086935).

Traditional molecular chemistry involves strong covalent bonds formed by the sharing or exchange of electrons between the atoms comprising a molecular system. Supramolecular chemistry involves systems that are held together by weaker, noncovalent connections, such as hydrogen bonds, electrostatic, and van der Waals forces. While nature uses supramolecular chemistry to form the double-helix of DNA or to fold proteins, this research team believes that these ideas could also be translated to nanotechnology, where single layers of 2D structurally ordered materials—such as graphene—could fulfill many requirements. The key is that they should be processed in solution.

“Solution-based processing allows for mass production and reduced manufacturing costs, and is an important step for transferring materials to a dry state without losing their structural integrity,” said Yi Liu, who oversees the supramolecular electronics research group at Berkeley Lab’s Molecular Foundry.



Supramolecular organic frameworks feature a porous framework with honeycomb periodicity similar to a metal-organic framework.

“Solution-based processing also allows for bio-related applications such as biomimetic sensing, where the framework structure is advantageous for the capturing of guest molecules and the amplification of chemical signals.”

However, the self-assembly of well-defined 2D supramolecular systems polymers in solution has been a challenge because such polymers tend to precipitate out of solution, making them difficult to manipulate and characterize. To meet this challenge, co-researcher

Zhan-Ting Li of Shanghai Institute of Organic Chemistry and Fudan University, China, and his collaborators used a combination of self-assembling tripods and macrocycle rings to form a porous framework with honeycomb periodicity, similar to that of a MOF, but which remains rigid in solution. Equipping the tripods with bulky hydrophilic groups that resist stacking preserved the solubility and single-layer 2D architecture of the framework.

“That our framework is held together by reversible, noncovalent supramolecular interactions ensures good solubility in water,” Li said. “The precise dimensional control of our solution-based processing facilitates the structural and chemical customization of our frameworks.”

The tripods of these SOFs were made from aromatic bipyridine molecules whose trio of struts or arms was interlocked with the struts of their neighboring molecules through the macrocycles,

which were made from cucurbituril molecules. The molecules used in this study were proof-of-principle starters. Other molecules for the struts could be employed in the future for the design of similar or more complex architectures.

Liu and his collaborators at the Molecular Foundry and in Shanghai are now working to create soluble SOFs in three dimensions.

Lynn Yarris

Nano Focus

Iron catalyst reservoir doubles CNT growth on alumina

The most common way to synthesize tall carpets of vertically aligned carbon nanotubes (CNTs) is to heat samples with thin films of iron (catalyst) on top of alumina (underlayer) in the presence of hydrocarbon gases at temperatures between 700°C and 800°C. Now researchers at Bar Ilan University (BIU) in Israel have shown how a thin film of iron positioned *below* the alumina underlayer can substantially affect the growth of CNTs. The results may also help solve the long-standing puzzle: what makes CNTs grow?

“The idea came after attending a presentation at a Materials Research Society Fall Meeting 2011, when Dr. Benji Maruyama explained how iron catalyst diffusion into the alumina underlayer was a factor in CNT growth termination. I thought that if the disappearance of iron on the top surface through porosity in the alumina is the cause for CNT termination, then we can replenish its supply from the bottom by using a reservoir of iron. We indeed doubled the growth but the underlying mechanism was very different from what we expected,” said Gilbert Daniel Nessim, principal investigator of this research, which was published in the February 7 issue of *Nanoscale* (DOI: 10.1039/C3NR05240K; p. 1545).

The researchers on Nessim’s team used the standard iron/alumina system as a benchmark. From the very first experiment, the new iron/alumina/iron reservoir system led to taller CNTs, with

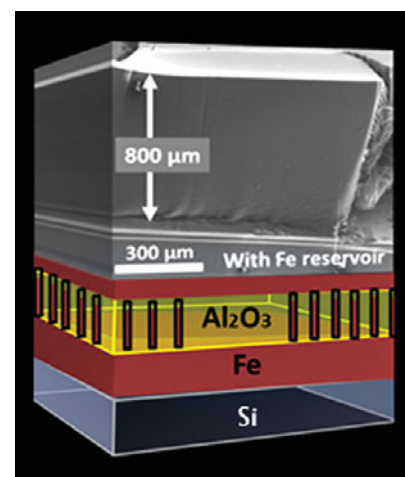
heights up to two times that of the iron/alumina system.

“From the start, the good results showed that we were onto something, but we started questioning the mechanism at play when we noticed that even very short growth experiments—30 seconds—led to taller CNTs on the sample with the iron reservoir,” said Efrat Shawat, a PhD candidate in the Nessim laboratory and lead author of their article. “It is only after extensive annealing experiments to observe the catalyst surface dewetting that we understood that the iron reservoir affected the morphology of the top surface,” she said.

Annealing experiments performed using samples with increasing thicknesses of the alumina layer gave the research team the clue to understanding this mechanism. As thicker alumina layers did not show the height enhancement factor, it appeared that pinholes in the alumina underlayer were key to understanding the mechanism at play.

“Only a few years back, observation of morphological size evolution of catalyst nanoparticles during CNT growth provided a significant hurdle to the realization of growing infinitely long, continuous CNTs,” said Cary Pint, an assistant professor of mechanical engineering at Vanderbilt University who, along with graduate student Landon Oakes, collaborated with the Bar Ilan researchers on this study. “Our work demonstrates that materials once neglected in playing any role in this process could be the key to overcome this hurdle.”

Shawat said that with the understanding of this new mechanism, the research



Schematic illustrating the migration of iron from the thin-film catalytic reservoir (iron) to the top surface of alumina through pinholes in the alumina layer. The resulting carbon nanotube carpets obtained are up to two times taller compared to the samples without the reservoir.

team now wants to study the effects of different reservoir materials on CNT growth. “For instance, we used a different non-catalytic metal and obtained interesting carpets with uniformly dispersed pores that we plan to use for battery electrode applications,” she said.

“By achieving taller CNT carpets, the throughput of the manufacturing process increases, and CNTs are more useful in applications that require longer CNTs and taller carpets,” said John Hart, associate professor at the Massachusetts Institute of Technology who was not involved in this research. “I look forward to potential future work integrating this method into applications,” he said.