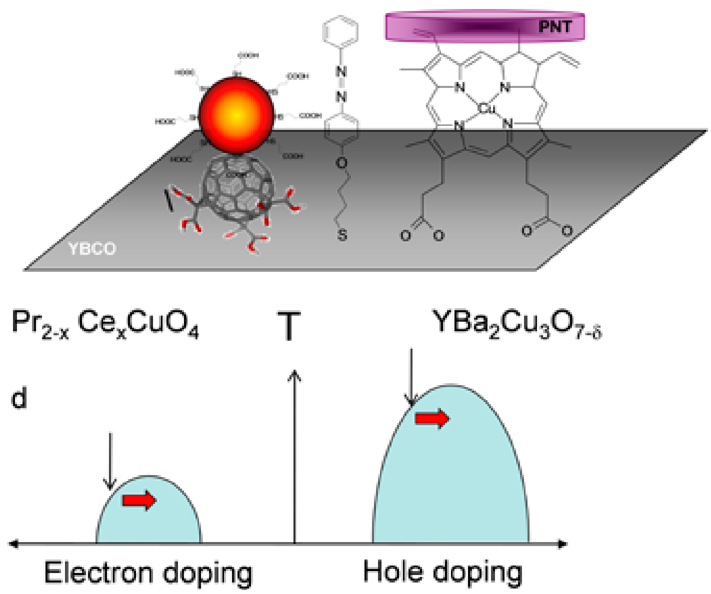
TEL AVIV UNIVERSITY
NANONEWS
Tel Aviv University Center for Nanoscience and Nanotechnology
Editors: Dr. Nava Ariel Sternberg and Prof. Koby Scheuer

Tuning the critical temperature of cuprate superconductor films using self-assembled organic layers

I. Carmeli[1], A. Lewin[2], E. Flekser[2], I. Diamant[2], Q. Zhang[3], J. Shen[3], M. Gozin[1], S. Richter[1] , and Y. Dagan[2]

[1]Raymond and Beverly Sackler School of Chemistry, Tel Aviv University
[2]Raymond and Beverly Sackler School of Physics and Astronomy, Tel Aviv University
[3]Shanghai Institute of Materia Medica (SIMM) Chinese Academy of Sciences

Many of the electronic properties of high-temperature cuprate superconductors (HTSC) are strongly dependent on the number of charge carriers put into the CuO_2 planes (doping). Superconductivity appears over a dome-shaped region of the doping-temperature phase diagram. The highest critical temperature (T_c) is obtained for the so-called "optimum doping". The doping mechanism is usually chemical; it can be done by cationic substitution. This is the case, for example, in $La_{2-x}Sr_xCuO_4$ where La^{3+} is replaced by Sr^{2+} thus adding a hole to the CuO_2 planes. A similar effect is achieved by adding oxygen as in the case of $YBa_2Cu_3O_{6+d}$ where d represents the excess oxygen in the sample. In this paper we report on a different mechanism, one that enables the addition or removal of carriers from the surface of the HTSC. This method utilizes a self-assembled monolayer (SAM) of polar molecules adsorbed on the cuprate surface. In the case of optically active molecules, the polarity of the SAM can be modulated by shining light on the coated surface. This results in a light-induced modulation of the superconducting phase transition of the sample. The ability to control the superconducting transition temperature with the use of SAMs makes these surfaces practical for various devices such as switches and detectors based on high-T_c superconductors.



Scheme 1. Schematic illustration of the various molecular films deposited on the HTCS. a, CF monolayer coated with CdS. b, AZ monolayer. c, Heterostructure SAM composed of porphyrin nanotubes (PNT) condensed on porphyrin monolayer. For a CF monolayer, upon addition of CdS, an increase in T_c is observed. Reversible T_c modulation has been achieved by an AZ monolayer and the porphyrin-based heterostructure. d. Phase diagram of the two superconductors used. The horizontal axis is the carrier concentration (n) or doping. The origin represents the undoped insulating compound. Moving to the left (or right) represents increasing electron (or hole) doping. Superconductivity is observed in the dome-shaped regions of this doping-temperature phase diagram. The shift on the phase diagram resulting from the SAM for both electron- (overdoped) and hole-doped (underdoped) cuprates is indicated by the red arrow. The SAM extracts electrons from both types of surfaces and this results in an increase in T_c.

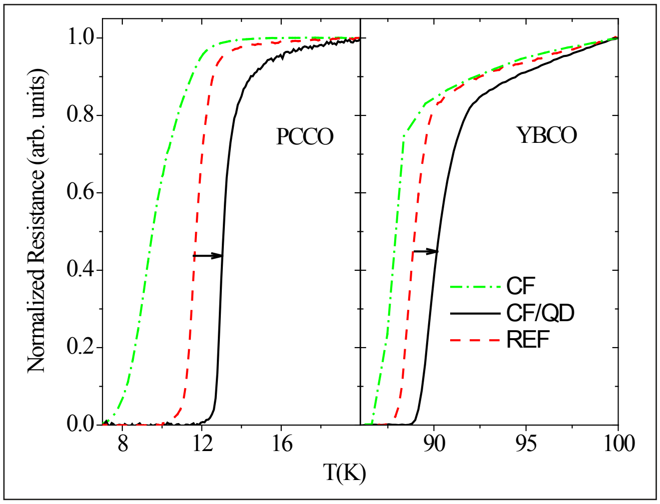


Figure 1. Normalized resistance measurement of CF coupled to CdS quantum dot on $Pr_{1.83}Ce_{0.17}CuO_4$ (left) and on $Y_1Ba_2Cu_3O_{7-d}$ (right) films. Bare film resistivities are about 80μW-cm at 100K for both samples. Adsorption of the CF SAM results in a decrease in T_c (black) compared to the uncoated reference sample (green) and CF/QD coated one (red line) where a remarkable increase in Tc is observed for both the electron- and hole-doped cuprates The observed enhancement of Tc corresponds to a charge transfer of ~0.1 carriers per unit cell. This is consistent with the change in surface potential found from KFM measurements.

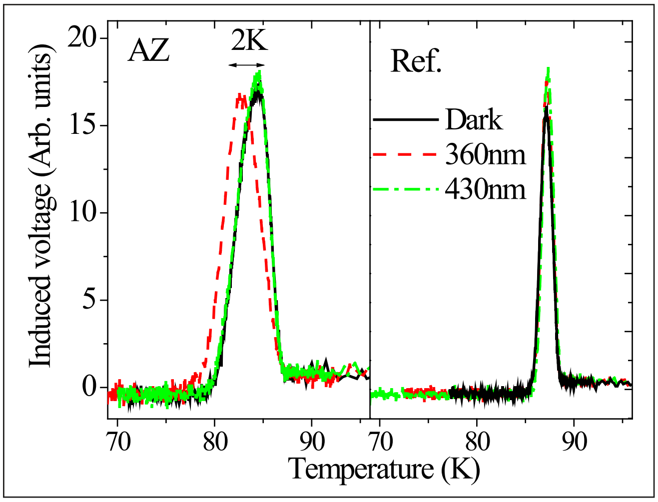


Figure 2. Reversible light-induced T_c switching of YBCO-coated AZ monolayer (left panel) compared to the null effect found in the SAM-free reference sample (right panel) measured by the imaginary component of the induced voltage in the AC susceptibility. Excitation by UV light (360nm) causes a 2K decrease in T_c while illumination with 430nm (red curve) increases Tc to its original value (black curve). Tc is defined by the peak in the signal. A clear reversible light-induced switching of Tc is observed compared to the null effect found in the SAM-free reference sample (see right panel). We attribute this effect to the conformational changes of the azobenzene ring accompanied by reversal of the molecule dipole induced by illumination.

In cuprate superconductors, Tc has an approximately quadratic dependence on carrier concentration.[1] The carrier concentration is an order of magnitude lower than that of metals and the screening is weaker. This raises the possibility of modifying the carrier concentration by applying an electric field to the surface. One approach was to use field-effect devices.[2, 3] Here we report on an alternative approach to doping the surface of the HTSC, namely with the use of a molecular self-assembly method.

A self-assembled monolayer (SAM) is an organized layer of molecules in which one end of the molecule, the binding group, is designed to interact favourably with the solid surface of interest, forming a well-organized monolayer on it.[4] The SAM is terminated with a functional group - in our case these are surface dipole-forming molecules or optically active moieties. The expected change in the work function due to a dipole moment of 1 Debye per molecule in a "typical" SAM with molecular density of 5´10^{14} cm^{-2} is ~0.5eV. The resulting electric field is compensated by charge transfer between the substrate and the SAM. The amount of charge transfer per molecule is q=μ/r, where *r* is the length of the molecule. When adsorbed on a cuprate surface, this charge transfer can be designed to induce holes and thus change the surface carrier density and the resulting critical temperature

We found that it is possible to modulate the number of charges in cuprate superconductor films by depositing a self-assembled monolayer on their surface. The monolayer is made of light-sensitive polar compounds, such as an azobenzene derivative, or nanostructures, such as a porphyrin–nanotube composite. On irradiation with light, charges are transferred from the cuprate oxide to the monolayer, resulting in a hole-doped superconductor with a different Tc. The process is reversed when the light is switched off.

This study clearly demonstrates that functional self-assembled monolayers can be used to control the Tc of superconductive cuprate oxides.

This project is the outcome of an internal collaboration within the Tel Aviv University Center for Nanoscience and Nanotechnology conceived during the annual meeting at "Hagoshrim". The novel approach for modulating Tc, based on the design of functional SAMs found in this research, may pave the way to making dissipationless electrical switches or functional devices for memory storage. This paper was published in Angewandte Chemie, 51, 1-5, April 2012.

References

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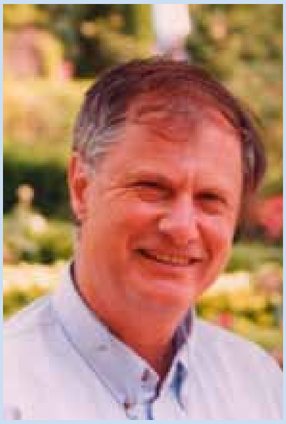
New director to the center



Prof. Ori Cheshnovsky

Center Director,
2004–2012

On Jan 31st Prof. Ori Cheshnovsky stepped down from his role as the Nanocenter director after over 7 years of heading the Nanoscience and Nanotechnology community at TAU. In February 2012, he has assumed the position of the Nanotechnology Center scientific committee chair replacing Prof. Guy Deutscher. Prof. Cheshnovsky joined TAU in 1981 after completing a postdoc in Harvard University. He received the "Distinguished young scientist" fellowship of Bat-Sheva de Rothschild between 1981-1983 and the "Distinguished young scientist" Alon fellowship between 1982-1984. Prof. Cheshnovsky became a full Professor in 1995 in the School of Chemistry, in the Faculty of Exact Sciences. Between 2001 and 2004 he served as the head of the Chemistry department and in 2004 became the Sackler chair for Clusters and Nanoparticles. In 2007 Prof. Cheshnovsky received the Weizmann Prize in Exact Sciences and in 2008 he became a fellow of the American Physical Society. Prof Cheshnovsky, an experimental Chemical Physicist, studies clusters, by utilizing noval methods, developed by him, in photoelectron spectroscopy focusing on identifing critical cluster size which support bulk properties. Recently he specializes in spectroscopy of nano-objectson nanoscale optics in STM Junctions and Electronic Properties of Clusters. Prof. Cheshnovsky was one of the first people promoting Nanotechnology in Israel serving in the "Bikura" committee of promoting nanoscience reserch (1997-2001), and served in the TELEM committee. He led the nano center in building labs, recruiting new nano researchers, supporting outstanding graduate student and postdocs in various nano related fields, as well as purchasing advanced and sophisticated equipment to facilitate excellent research in Nanoscience and Nanotechnology at TAU. He initiated and headed the forum of nano centers in Isarel. On behalf of the TAU nano community, we would like to thank Prof. Cheshnovsky for his seminal contribution to the center and to nano research and the nano community at TAU in general.

Prof. Yael Hanein

Center Director,
2012–

Beginning February 1st, 2012, Prof. Yael Hanein assumed the position of the Nanocenter director. Prof. Hanein is an Associate Professor in the Iby and Aladar Fleischman Faculty of Engineering, School of Electrical Engineering, Department of Physical Electronics. Her research is focused on developing novel micro and nanofabrication techniques for biological applications. Prof. Hanein joined TAU in 2003 after completing her postdoctoral research at the University of Washington, Seattle, WA. She was awarded a David Kulitz fellowship at Tel-Aviv University between 2004 and 2006. Prof. Hanein was selected as an Outstanding Young Scientist by the IAP for the second conference for young scientists of the world economic forum "summer Davos" in 2009 and as the Young Mentor for the IAP's third and fourth conferences. Prof. Hanein is a core member of the Nanoscience and Nanotechnology center from its early days, as well as an active member of the Scientific committee of the center. Prof. Hanein led, together with Prof. Ori Cheshnovsky, the establishment of MNCF, the micro and nano central characterization and fabrication facility at TAU, which today provides services to numerous research groups as well as industrial companies. In addition to her extensive academic activity Prof. Hanein holds a key position in a start-up company in the field of Bio-Med and is a member of several consortia with industrial partners.

The Nanoscience and Nanotechnology community wishes Prof. Hanein success in her new and important role.

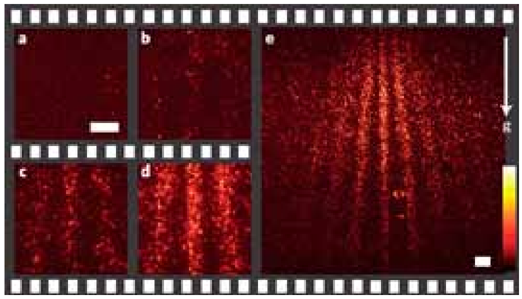
Research news

Real-time single-molecule imaging of quantum interference

Alexander Tsukernik, Ori Cheshnovsky, et al.

The observation of interference patterns in double-slit experiments with massive particles is generally regarded as the ultimate demonstration of the quantum nature of these objects.

Such matter–wave interference has been observed for electrons, neutrons, atoms, and molecules and, in contrast to classical physics, quantum interference can be observed when single particles arrive at the detector one by one. The build-up of such patterns in experiments with electrons has been described as the "most beautiful experiment in physics". In the paper, published in Nature Nanotechnology, it is shown how a combination of nanofabrication and nano-imaging allows to record the full two-dimensional build-up of quantum interference patterns in real time for phthalocyanine molecules and for derivatives of phthalocyanine molecules, which have masses of 514 AMU and 1,298 AMU respectively. A laser-controlled micro-evaporation source was used to produce a beam of molecules with the required intensity and coherence, and the gratings were machined in 10-nm-thick silicon nitride membranes to reduce the effect of van der Waals forces. Wide-field fluorescence microscopy detected the position of each molecule with an accuracy of 10 nm and revealed the build-up of a deterministic ensemble interference pattern from single molecules that arrived stochastically at the detector. In addition to providing this particularly clear demonstration of wave–particle duality, our approach could also be used to study larger molecules and explore the boundary between quantum and classical physics. This paper was published in Nature Nanotechnology, 34, 1-4, March 2012. Experiments were performed in the University of Vienna in collaboration with TAU, the University of Basel, and Karlsruhe Institute of Technology.

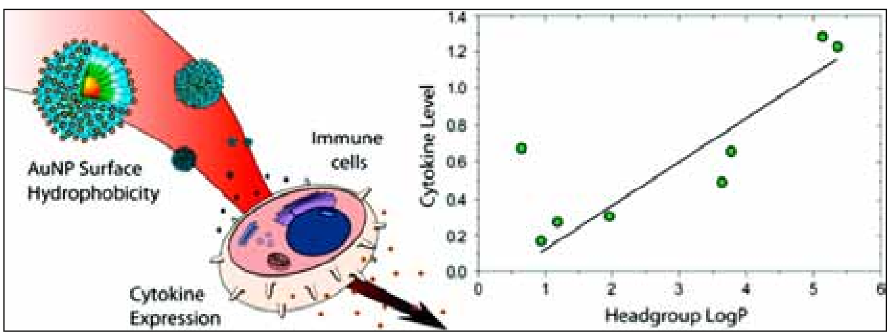


Build-up of quantum interference. **a–e**, Selected frames from a false-color movie recorded with an EMCCD camera showing the build-up of the quantum interference pattern for PcH2 molecules. Images were recorded before deposition of the molecules (**a**) and 2min (**b**), 20 min (**c**), 40 min (**d**) and 90min (**e**) after deposition. Scale bars, 20 mm (**a–e**). The color bar ranges from 25 to 120 photons in **a–d** and from 220 to 650 photons in **e**. **a–d** are taken from Supplementary Movie 1, and the wide-field view in **e** is taken with the same objective as Supplementary Movie 2. The movie frame rate was 0.1 Hz for the first 20 min (**a–c**). Thereafter it was reduced to 0.05 Hz to allow for another dynamic equilibrium of bleaching and the arrival of fresh molecules. Collimation slit S (Fig. 1) was cut into a 50-nmthick SiN membrane and had dimensions of 1 mm (width) and 100 µm (height). Diffraction grating G was cut into a 10-nm-thick SiN membrane (width, 5 µm; height, 100 µm), with period *d*=100 nm. Width of the individual slits: s=50 nm. L_1=702 mm, L_2=564 mm. The arrow pointing downwards indicates the direction of the gravitational acceleration *g*.

Nanoparticle hydrophobicity dictates immune response

Meir Goldsmith, Dalit Landesman–Milo and Dan Peer

Understanding the interactions of nanomaterials with the immune system is essential for the engineering of new macromolecular systems for in vivo applications. Systematic study of immune activation is challenging due to the complex structure of most macromolecular probes. In collaboration between Vince Rotello's Lab at the University of Massachusetts and Dan Peer's laboratory of Nanomedicine at Tel Aviv University, the researchers have used engineered gold nanoparticles to determine the sole effect of hydrophobicity on the immune response of mouse splenocytes. The gene expression profile of a range of cytokines (immunological reporters) was analyzed against the calculated LogP of the nanoparticle headgroups, with an essentially linear increase in immune activity with the increase in hydrophobicity observed in vitro. Consistent behavior was observed with in vivo mouse models, demonstrating the importance of hydrophobicity in immune system activation. In addition, it was observed that tiny gold particles (2 nm in diameter) decorated with different hydrophobic moieties induce cytokine expression, which is in oppose to the current dogma that small particles (< 50 nm in diameter) are considered as stealth particles, shielded from the immune system. The paper is now on line in the Journal of the American Chemical Society.



Prizes and Awards

- **Ben Maoz**, a PhD student in the group of Prof. Gil Marokvich won the best student talk at the IMEC 15 conference, Dead Sea, 2012.

- **Prof. Koby Scheuer** from the School of Electrical Engineering received a 750k$ grant from DARPA for the development of nano-sensors.

- **FTA** – A group of researchers, led by **Dr. Dan Peer** was awarded focal technology area grant of $11.5M, given by INNI, for "Nanomedicines for Personalized Theranostics". Other members of the group are Prof. Ehud Gazit, Dr. Ronit Satchi-Fainaro, Prof. Rimona Margalit, Prof. Moshe Portnoy, Prof. Yoni Leor, Prof. Itai Benhar and Prof. Doron Shabat, in addition to collaborators from other institutes. The group's research will focus on developing novel platforms for theranostics of angiogenesis-dependent. These are diseases characterized by the formation of new blood vessels from pre-existing vasculature, such as cancer, inflammatory bowel diseases, and cardiovascular diseases.

- **Dr. Oded Hod** was elected as a member of the Global Young Academy (GYA).

- **Mark Shein**, a PhD student in the group of Prof. Yael Hanein won the Adams Super Center for Brain Studies award for the best poster presentation at the Brain Plasticity Symposium, TAU 2012.

- **Elad Mentovich**, a PhD student in the group of Dr. Shachar Richter won two international prizes; During the last Materials Research society Meeting which was held in Boston Elad won a silver medal in the student award competition. In the recent conference of the European Material Research Society, held in Strasburg, Elad was awarded an additional student excellence prize.

New equipment at the center

Micro-spectroscopy system

The system is a Fourier Transform (FT) Visible-Near IR spectrometer combined with a cooled CCD camera mounted on the camera port of a standard upright Olympus BX51 microscope. The system is produced by Applied Spectral Imaging (http://www.spectral-imaging.com).

The spectrometer records the FT spectrum of a region of interest within the field of view of the camera at every pixel of the camera. The result is a 3D data array where the x-y plane is the spatial coordinates of the region and the third dimension is the wavelength. Since the microscope is equipped with bright/dark field capabilities both in transmission and reflection + basic epi-fluorescence, spatially resolved spectroscopy can be done at each of these modes.

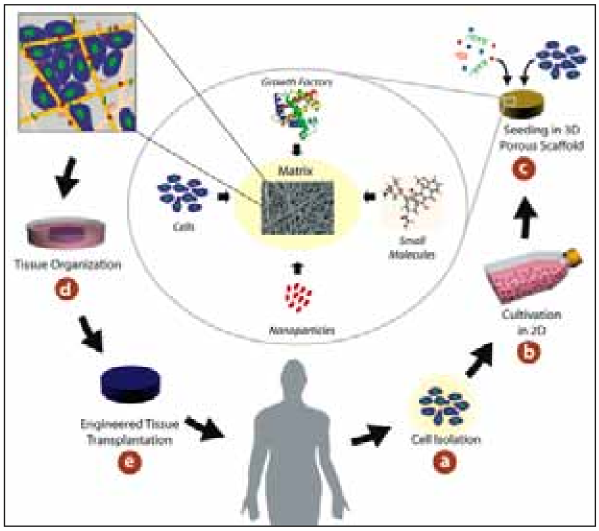
The spectral resolution varies from about 8-10 nm on the blue edge (400 nm) to around 20 nm at the NIR edge (~1000 nm).

The software allows various types of data processing, where the main mode is usually averaging the spectra over a selected number of pixels and doing mathematical operations on the spectra taken at different regions, in particular with respect to a selected background spectrum. The system is located in room 25 in the nano center under the supervision of Prof. Gil Markovich.

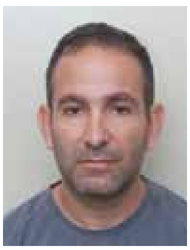
New researchers in the Center

Dr. Tal Dvir

Dr .Tal Dvir from the Department of Biotechnology established the Laboratory for tissue engineering and regenerative medicine. Tissue engineering has evolved as an interdisciplinary technology combining principles from the life, material, and engineering sciences with the goal of developing functional substitutes for damaged tissues and organs. Rather than simply introducing cells into a diseased area to repopulate a defect and/or restore function, in tissue engineering the cells are often seeded in or onto biomaterials before transplantation. These materials serve as temporary scaffolds, mimicking the natural extracellular matrix, and promote the reorganization of the cells to form a functional tissue (see figure). The Dvir lab develops new biomaterials that recapitulate the nanocomposite nature of the extracellular matrix, investigates the impact of nanostructures on the properties of scaffolds and on the behavior of engineered cardiac and neuronal tissues. The lab also fabricates and uses various electronic and nonelectronic nanodevices to monitor and trigger certain processes during stem cell differentiation and tissue development in vitro, and to follow the performances of engineered tissues post implantation.

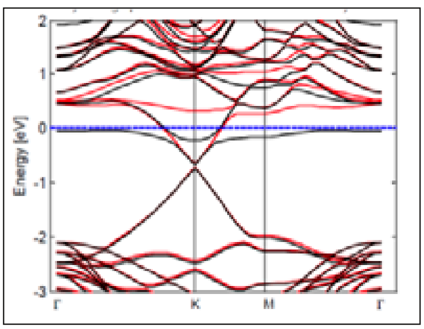


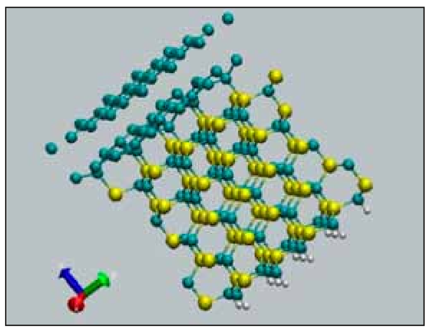
Dr. Amir Natan



Dr. Amir Natan joined the school of Electrical Engineering after completing a post-doc in Northwestern University. Dr. Natan is using first principles quantum calculations and other tools to investigate the electronic properties of materials and devices. Commercial and public software are used in parallel to the development of in-house software and new theoretical methods in the field. The lab's research includes: *properties of novel materials* – structural and electronic properties of novel materials (e.g. chemically modified Graphene or novel metal-oxides). Main efforts are in the fields of finding novel materials and devices for energy storage (batteries) and photovoltaic applications. Other topics are: *interaction of light with matter* – non-linear effects in molecules and nano-structures, photovoltaic cells, and electrons dynamics in systems. The methods used are *multi-scale modeling of materials and devices* – developing theoretical methods to integrate first principles calculations with macroscopic and intermediate scale models. *Physical phenomena at surfaces and interfaces* – research of emerging phenomena of materials with different dimensionality or at interfaces, especially electric and magnetic properties at interfaces. *New theoretical and numerical methods* – different methods to achieve faster and more exact calculations are explored. In parallel to algorithm development and implementation the group also studies the use of special purpose hardware such as graphical processor units (GPUs).

The lab research facility includes a 200 cores cluster (to be expanded soon). Dr. Natan is participating as a new recruit in the Petroleum Alternatives for Transportation (PAT) excellence center and as a regular member in the Focal Technology Area (FTA) Nano initiative for new materials development for photovoltaic applications.





A model of graphene on silicon-carbide surface, to the right – the resulting band structure of the model.

Events

- **Nanobit and TAU** – Nanobit is a new group within Elbit Systems ltd designated to advance R&D in Nanotechnology in applications relevant to the company. A successful workshop was held on January 22nd in which thirteen researchers affiliated with the center presented their research to technical crowd from Elbit Systems.

- **Industry day** was held on May 29th. Technology, MNCF news, and networking. Technological talks were delivered by MNCF staff to industrial collaborators and colleagues.

- **The Fred Chaoul 8th annual workshop** is to take place on 26th-28th of June 2012, in Hagoshrim hotel and conference center. Cutting edge research advances and accomplishments will be presented by leading researchers in diverse fields of nanoscience and nanotechnology. The keynote presentations of the workshop will be given by: Prof. David A. Weitz, Harvard University, USA, Prof. Viola Vogel, ETH, Switzerland, and Alex Zunger, University of Colorado, Boulder, USA.

New faces at the Center

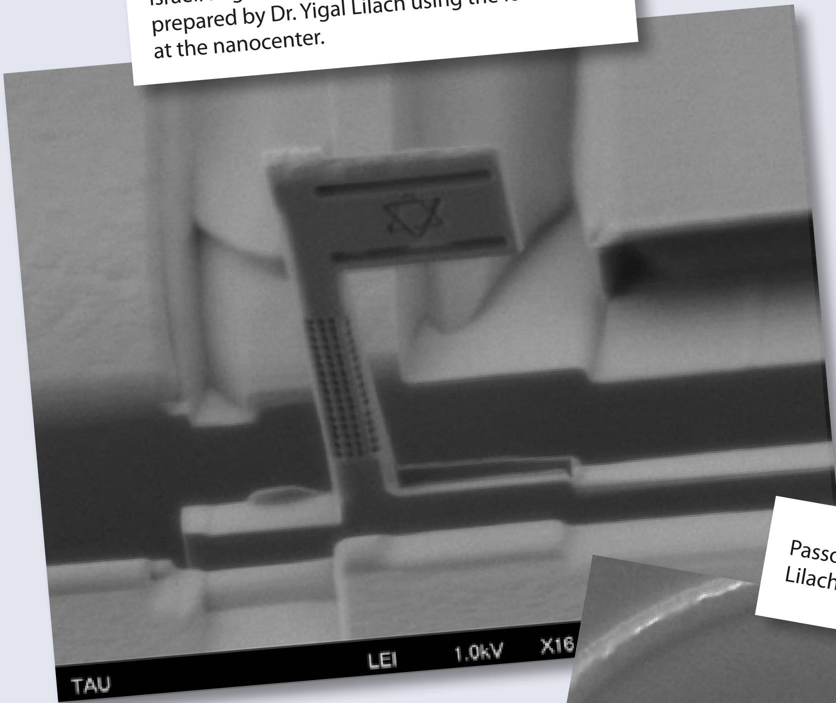
Dr. Yigal Lilach

Dr. Yigal Lilach has finished his PhD in photochemistry on metallic surfaces in 2003. Between 2003 and 2006 he held a post-doc position in UCSB and PNNL, and in 2007 he joined the nanofabrication unit in the Hebrew University in Jerusalem. Starting from July 2011 he is managing the SEM, e-beam, and FIB lab at the center, replacing Dr. Alex Zukernik.

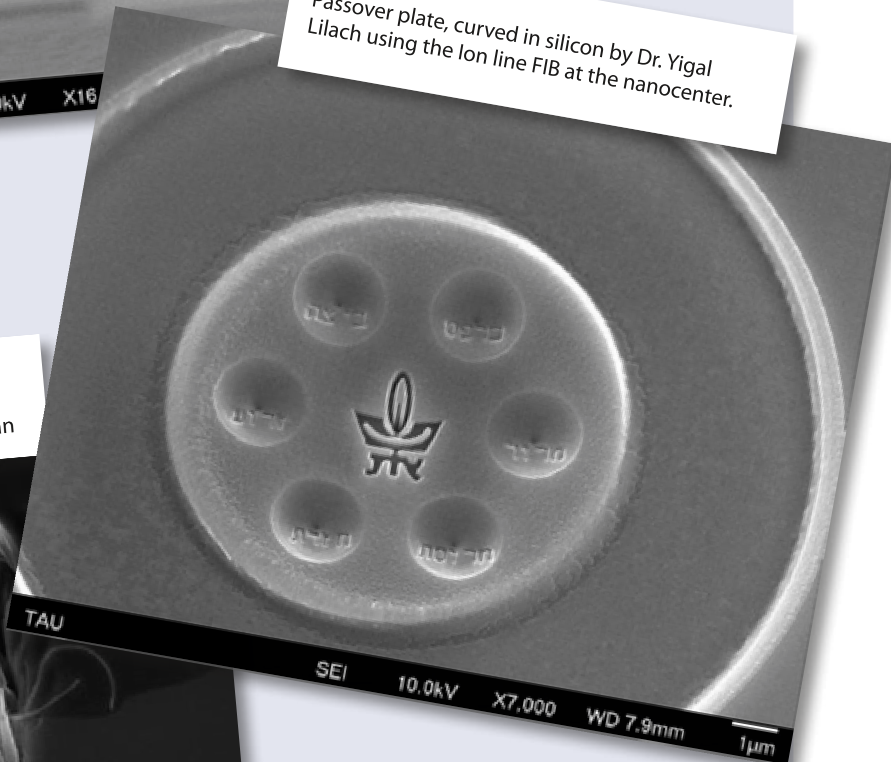
Dr. Nava Ariel Sternberg

After completing a Ph.D. in electronic materials and working several years at the industry; at Intel Corporation and at Elbit systems – ElOp, Dr. Ariel-Sternberg joined TAU professional staff in September 2011 as the Micro and Nano Central Characterization and Fabrication facility general manager. On December 2011 she became the managing director of the Nano center replacing Dr. Moshe Evenor.

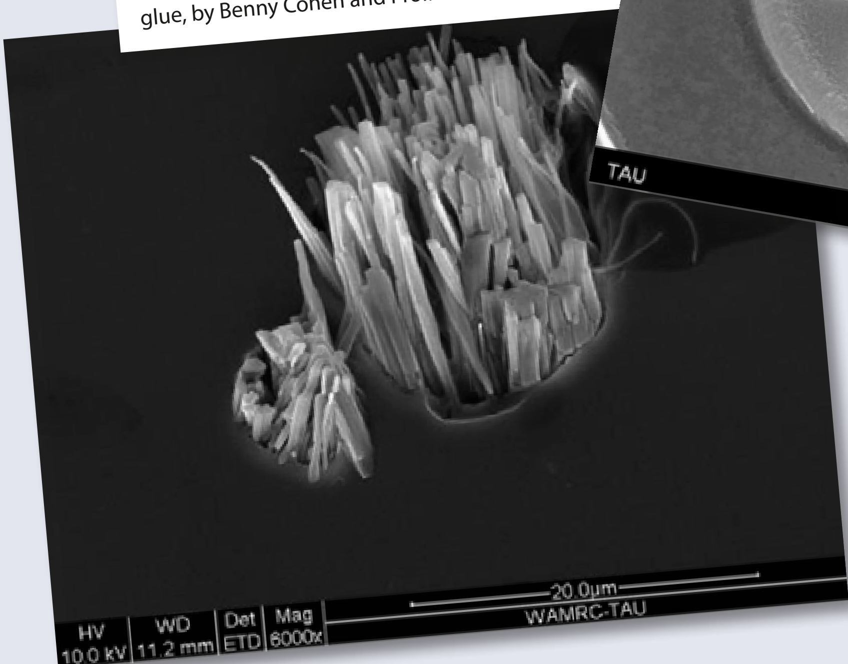
Israeli flag curved in silicon with 64 dots prepared by Dr. Yigal Lilach using the Ion line FIB at the nanocenter.



Passover plate, curved in silicon by Dr. Yigal Lilach using the Ion line FIB at the nanocenter.



The winning photo in the nano photo competition: Drug crystallization in a medical glue, by Benny Cohen and Prof. Meital Zilberman



http://nano.tau.ac.il