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Metal-Directed Assembly and Metal-Organic Frameworks: ICS Symposium Honoring Wolf Prize Laureates Makoto Fujita and Omar M. Yaghi, May 30, 2018, Technion – Israel Institute of Technology, Haifa, Israel

Ehud Keinan*^[a]

The Annual Wolf Prize Symposia of the ICS have become a significant part of the scientific landscape of the State of Israel. These highly attended events occur annually in late May or early June during the Wolf Prize week, usually one day before the Wolf Prize award ceremony in the Knesset.

Every symposium features a busy day of excellent lectures presented by the Wolf Prize Laureates and other esteemed speakers who are active in the field of the prize and/or related to the Laureates' research groups. The symposia take place in one of the university campuses. For example, the 2012 symposium, "Celebrating Nanochemistry", held in Tel Aviv University, was dedicated to A. Paul Alivisatos and Charles M. Lieber. The 2013 symposium entitled "New Biomaterials for Therapy" was held in Ben-Gurion University in honor of Robert Langer. The 2014 symposium honoring Chi-Huey Wong, entitled "Chemical Biology and Biomedical Science" was organized at the Schulich Faculty of Chemistry of the Technion. In 2015 no Wolf Prize in chemistry was awarded. The Technion hosted also the 2016 Wolf Prize symposium entitled "Chemical Synthesis and Drug Discovery"^[1] in honor of the Prize Laureates K. C. Nicolaou and Stuart L. Schreiber. In 2017 the symposium, entitled "Organometallics and C–H Activation",^[2] honoring Wolf Prize Laureate Robert G. Bergman was held in the Technion as well.

The 2018 event (Figure 1), organized by the ICS President Ehud Keinan and Project Manager Liraz Maanit, was generously sponsored by the Technion, the Schulich Faculty of Chemistry, the Berkeley Global Science Institute, Rigaku Corporation of Japan, Tokyo Chemical Industry (TCI) Co., and Merck Sharp & Dohme (MSD) Corporation.

Opening Session

Prof. Ehud Keinan opened the symposium and greeted the audience. "Welcome everybody, particularly the Wolf Prize laureates Fujita and Yaghi, Sir Fraser Stoddart, all other

speakers, chairpersons, Rabbi Prof. Daniel Hershkowitz, distinguished guests. For the past three decades the ICS has upheld the tradition of holding organizing the Wolf Symposia in Israel. Every one of these has been a very exciting event for me and I am sure that it is so for all of you.

There are three messages I wish to convey this morning.

My first comment refers to the Wolf Prize itself. When Ricardo Wolf initiated this Prize, probably thinking of a "Jewish Nobel Prize", as it is nicknamed today, I doubt that he imagined how far this prize could go. Most people agree that this is the second most important prize after the Nobel, particularly in chemistry. Certainly, many agree about its predicted Nobel-predicting power, for which we have a convincing track record. As a member of the Wolf council, I can tell you that we consider as strong candidates those who have a good chance to proceed later on to Stockholm. And many people know that the road to Stockholm goes through Jerusalem.

It is appropriate to say a few words about Ricardo Wolf, an inventor, diplomat, and philanthropist. He was born in Hanover in 1887, and emigrated from Germany to Cuba before the First World War. In 1924, he married the tennis champion Francisca Subirana. For many years, Ricardo Wolf and his brother Sigfried Wolf worked to develop a process for recovering iron from smelting process residue. Their invention was utilized in steel factories worldwide, bringing him considerable wealth. Wolf lent both moral and financial support to Fidel Castro from the onset of the Cuban revolution. Beholden to Ricardo Wolf for his unswerving support, and cognizant of his personality and natural gifts as a diplomat, the Cuban leader offered him the position of Minister of Finance and, after Wolf declined, responded to Wolf's request and appointed him Cuban Ambassador to Israel in 1961. Wolf held this position until 1973, the year Cuba severed diplomatic ties with Israel. Upon relinquishing his diplomatic post, Wolf decided to remain in Israel, until his death in 1981. In 1975, Ricardo Wolf established the Wolf Foundation, and the Wolf Prizes have been awarded since 1978 in six fields: Agriculture, Chemistry, Mathematics, Medicine, Physics. The Arts prize rotates annually between architecture, music, painting and sculpture. Each prize consists of a diploma and US\$100,000.

The second comment I wish to make is that science is highly international and many scientists emigrate to other

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Metal-Directed Assembly and Metal-Organic Frameworks

ICS Symposium Honoring Wolf Prize Laureates
Makoto Fujita and Omar M. Yaghi

May 30th, 2018



Technion, Schulich Faculty of Chemistry, Hall 1

- 08:30-09:00** **Gathering and Registration**
- 09:00-09:30** **Opening session**
Prof. Ehud Keinan, Technion, President, Israel Chemical Society
Prof. Adam Schwartz, Technion, Senior Executive Vice President
Prof. Daniel Hershkowitz, Technion, Chairman, National Council of R&D
Prof. Sir James Fraser Stoddart, Northwestern University Evanston, IL, USA
- Session 1** **Chair: Prof. Ehud Keinan**, Technion, President, Israel Chemical Society
- 09:30** **Prof. Makoto Fujita**, University of Tokyo, Japan
Coordination Self-Assembly: From the Origins to the Latest Advance.
- 10:00** **Prof. Omar M. Yaghi**, University of California, Berkeley, CA, USA
Covalent Chemistry Beyond Molecules.
- 10:30** **Prof. Sir James Fraser Stoddart**, Northwestern University Evanston, IL, USA
Materials Beyond Cyclodextrins: Emergence Opens up a Whole New World of Wonders.
- 11:00-11:30** **Coffee Break**
- Session 2** **Chair: Prof. Maya Bar Sadan**, Ben-Gurion University of the Negev, Israel
- 11:30** **Prof. Kimoon Kim**, Pohang University of Science and Technology, Pohang, Korea
Nanostructured materials by covalent self-assembly.
- 12:00** **Prof. Meir Lahav**, Weizmann Inst. of Science, Rehovot, Israel
Understanding Electrofreezing at the Molecular Level with Pyroelectric Crystals.
- 12:30** **Prof. Lars Öhrström**, Chalmers University of Tech., Gothenburg, Sweden
Designing, Describing and Disseminating New Materials using the Network Topology Approach.
- 13:00-14:00** **Lunch Break**
- Session 3** **Chair: Dr. Sharon Ruthstein**, Bar Ilan University, Israel
- 14:00** **Prof. Laura Gagliardi**, University of Minnesota, Minneapolis, MN, USA
Computational Design of Functionalized Metal-Organic Framework Nodes for Catalysis.
- 14:30** **Prof. Yoram Cohen**, Tel Aviv University, Israel
Diffusion NMR in Supramolecular Systems and Beyond.
- 15:00** **Prof. Qing-Fu Sun**, Fujian Institute of Research, Fuzhou, Fujian, China
Lanthanide Organic Polyhedra.
- 15:30-16:00** **Coffee Break**
- Session 4** **Chair: Dr. Galia Maayan**, Technion - Israel Institute of Technology
- 16:00** **Prof. Tomohisa Sawada**, University of Tokyo, Japan
Concerted folding-and-assembly of short peptides via coordination.
- 16:30** **Prof. Milko E. van der Boom**, Weizmann Inst. of Science, Rehovot, Israel
Made in Israel: Metallo-Organic Materials and Devices.
- 17:00** **Prof. Xiao-Yu Cao**, Xiamen University, Fujian Province, China
Molecular Face-Rotating Polyhedra.
- 17:30** **Prof. Takuzo Aida**, University of Tokyo, Japan
Smart Soft Materials Fabricated under Nonequilibrium Conditions.
- 18:00** **Concluding remarks**



Organizer: Prof. Ehud Keinan **Registration:** Liraz Maanit israelchemistry@gmail.com

Figure 1. Announcement poster of the 2018 Wolf Prize Symposium autographed by all speakers.

countries, developing their careers far away from their homeland. It is not surprising that the country of affiliation of most of the 13 lecturers of this symposium is different from their country of birth. These scientists represent 6 countries (Japan, USA, Israel, China, Korea and Sweden) but they were born in 11 different countries (Figure 2). The USA as well as Israel enjoy immigration of great scientists although we Israel also suffer from the brain drain phenomenon. This continuous exchange of scientists is very good for science and very good for the country.

The third comment is about relates to the topics highlighted by the 2018 Wolf Prize in Chemistry. I tend to identify two fundamental cultures of scientific disciplines. In the first type, including astronomy, zoology and most fields of biology, the scientists are primarily discoverers. Practitioners of the second culture behave like architects – creating new objects and new systems. I consider most chemists as architects, certainly Fujita and Yaghi, as well as Stoddart and all other speakers of this symposium who are all architects at the molecular scale. And it is very interesting to look at this issue from the perspective of time. Architecture is a very old endeavor, probably older than 10,000 years. The visual arts are even older. Considering the fact that molecular sculpture and synthetic chemistry are less than 200 years old, we are witnessing just the beginning of chemical architecture and chemical arts.

Finally, since neither the Dean of the Faculty of Chemistry nor the President of the Technion could attend this symposium, I would like to say a few words about the Schulich Faculty of Chemistry. It was established by David Ginsburg in 1954 in the old building in downtown Haifa and moved to this campus 10 years later. Currently the faculty consists of 27 research groups, 240 undergraduate students in three tracks, 130 graduate students and 60 postdocs and senior researchers.

Since this symposium has been organized by the Israel Chemical Society I'd like to provide some basic information about the ICS, which was established in 1933. The community of Israeli chemists is quite small – probably less than 12,000 including chemical engineers and chemistry teachers. But the survival and further development of this country is highly dependent on these people because 40% of all industrial production and 25% of all exports are chemicals. We are very proud of the fact that 6 Israeli citizens have won the Nobel Prize in Chemistry within one decade. It was very rewarding for me that the Israeli Philatelic Service agreed to collaborate with the Israel Chemical Society and accept my graphic proposals, issuing 4 colorful Israeli stamps that commemorate those Nobel prizes in chemistry (Figure 3). As of today, The State of Israel has had 10 Presidents two of whom were scientists. It is not surprising that both of them, Chaim Weizmann and Efraim Katzir, were professors of chemistry.

Finally, I wish to thank the generous sponsors who made this event possible, including the Technion, the Schulich Faculty of Chemistry, the Berkeley Global Science Institute, Rigaku Corporation of Japan, Tokyo Chemical Industry (TCI) Co., and Merck Sharp & Dohme (MSD) Corporation. I am

grateful to the people who assisted me, particularly the ICS Project Manager Liraz Maanit, Reut Yinon Berman and Michal Bornstein, both from the Wolf Foundation, as well as people from the Schulich Faculty of Chemistry, among them Meital Barron and Zion Hai.

I would like to invite my colleague and friend, Rabbi Prof. Daniel Hershkowitz, who was Dean of Mathematics at the Technion at the time I served as Dean of Chemistry, so we know one another for a long time. Further on in his career Prof. Hershkowitz became Minister of Science and Technology, served as President of Bar Ilan University and is currently Chairman of the National Council of Research and Development."

Prof. Daniel Hershkowitz greeted the prize winners, speakers and audience, "I am very happy to be here with you at this happy occasion. Ehud has mentioned that I serve as Chairman of the National Council of R&D. This Council was appointed by the State President and its role is to advise the government on the policy of research and development in the future. In other words, we are asked to predict the future of science, which is essentially impossible. I remember that when I started my career in politics, we used to say that in the Middle East, it is very difficult to predict anything, especially the future. It is very difficult to say where science is going, not only in the next generation, but even in the next five years or so. Nevertheless, some predictions about scientific developments were successful, and one good example is the area of nanotechnology. This area started developing in Israel about 20 years ago and was strongly promoted over the past 10 years by the national effort on nanotechnology with massive government investments. That initiative has become a success story in terms of academic research in all universities and many commercial applications that resulted from that activity.

I think that both of our new Wolf Prize Laureates who have designed special new materials, represent the broad field of nanotechnology as well. I'm very happy to congratulate the two winners, Fujita and Yaghi, and hope that they will continue their scientific collaboration with many Israeli scientists. I also congratulate the Schulich Faculty of Chemistry, which is a national as well as international leader in chemistry, for hosting this important symposium. Prof. Keinan has mentioned the 6 Nobel Prize Laureates in Chemistry. As a mathematician, I wish to mention a 7th scientist, Professor of Mathematics Israel Robert Aumann of the Hebrew University of Jerusalem who received the Nobel Prize in Economic Sciences in 2005 for his work on conflict and cooperation through game-theory analysis.

I strongly believe that the language of science bridges the gaps between nations, religions and people. That's the language that we can all speak and we can all understand. So, I'm very happy about this special event. I wish all participants an enjoyable day and wish that all of us continue being part of this changing world of science."

Sir Fraser Stoddart greeted the audience and the laureates: "Good morning everyone. And good morning to our distinguished Wolf Prize laureates, Omar Yaghi and Makoto



Figure 2. Countries of affiliation and countries of birth of the symposium lecturers, represented by their national flags.

Fujita. I think it can be said that when you have really great scientists, they are likely to define their own arenas in science

and to that extent they leave a stamp which is uniquely theirs. I think we'll be in no doubt this morning when subsequently



Figure 3. The six Israeli scientists who became Nobel Prize Laureates, from left: Avram Hershko (2004), Aharon Ciechanover (2004), Ada Yonath (2009), Dan Shechtman (2011), Michael Levitt (2013), Arieh Warshel (2013) and the 4 Israeli stamps that commemorated those prizes and the International Year of Chemistry (2011), International Year of Crystallography (2014), and International Year of light (2015).

both laureates will demonstrate these notions in their presentations. I'm not going to take very much of your time, just want to mention that I think I first met Makoto at a Gordon conference in 1995. He tells me now that Omar Yaghi was also there but he was probably very quiet that time. It was a poster by Makoto that actually brought the message to me. He was a young scientist who was on his route to do great things. I'll just mention that his poster revealed that he was already building squares in a highly original way and later went to triangles and to rectangles and so on and so forth, and we became fascinated by the size of the cages that he produced. And most recently, an incredible method of using conventional crystallography to analyze these cages. I think that was a stroke of a genius.

With Omar I think I've met up in a conference in Oregon in October 2000. I think you were organizing a workshop. When you came to talk to me it was clear to me that you were kind of special. He brought to the chemical world a lexicon of abbreviations that were as lasting as DNA and NMR, including MOFs and COFs and reticular chemistry, and many more to come. The last thing I want to mention is that this science has opened great opportunities of commercial applications and large-scale synthesis of these materials, capturing water, carbon dioxide, etc.

I want to congratulate both of you. You raised my level of excitement in every way. I feel this is a new chemistry. This is a chemistry that has obvious novelty and originality. I think this is one of the youngest sciences. It has enormous ability to

recreate itself in a matter of months. I think this is what has happened, in an incredible way, within the last 2 decades. We should not forget the fact that this is a new science, not an old field. Congratulations."

Before starting the scientific program, Prof. Keinan, as ICS President, awarded seven of the foreign speakers with a lifetime Honorary Membership of the Israel Chemical Society: Makoto Fujita, Kimoon Kim, Lars Öhrström, Laura Gagliardi, Tomohisa Sawada, Xiao-Yu Cao and Takuzo Aida. Two of the guests, Sir J. Fraser Stoddart and Omar M. Yaghi have already received this recognition on a previous occasions.

Plenary Lectures

The scientific program included 12 plenary lectures, which were grouped in 4 sessions (Figure 4).

Makoto Fujita of the University of Tokyo and Institute for Molecular Science, lectured on "Coordination Self-Assembly: From the Origins to the Latest Advances." He explained that molecular self-assembly based on coordination chemistry has made an explosive development in recent years. Over the last more than 25 years, we have been showing that the simple combination of transition metals with bridging organic ligands gives rise to the quantitative self-assembly of nanosized, discrete and infinite frameworks. Representative examples include square molecules (1990), square grid sheets (1994), linked-ring molecules (1994), cages (1995), capsules (1999),



Figure 4. Collage of photos from the Wolf Prize Symposium. The Schulich Faculty of Chemistry, Technion, May 30, 2018. Photos by Avia Haberman, Micha Brickman.

swellable networks (2002), and tubes (2004) that are self-assembled from simple and small components. Originated from these earlier works, current interests in the Fujita group focus on i) molecular confinement effects in coordination cages, ii) solution chemistry in crystalline porous complexes (as applied to “crystalline sponge method”, 2013), and iii) giant self-assemblies (2016).

Omar M. Yaghi of the Department of Chemistry, Kavli Energy NanoScience Institute, Berkeley Global Science Institute, University of California at Berkeley, lectured on “Covalent Chemistry Beyond Molecules.” He pointed out that linking molecular building units by strong bonds to make crystalline extended structures (Reticular Chemistry) has given rise to metal–organic frameworks (MOFs) and covalent organic frameworks (COFs), thus bringing the precision and versatility of covalent chemistry beyond the atoms and molecules. The key advance in this regard has been the development of strategies to overcome the “crystallization problem”, and the use of metal-oxide clusters as secondary building units to impart unprecedented structural robustness, high surface area, and permanent porosity. To date, thousands of MOFs and COFs are made as crystalline materials. The molecular units thus reticulated become part of a new environment where they have (a) lower degrees of freedom because they are fixed into position within the framework; (b) well-defined spatial arrangements where their properties are influenced by the intricacies of the pores; and (c) ordered patterns onto which functional groups can be covalently attached to produce chemical complexity. The notion of covalent chemistry beyond molecules is further strengthened by the fact that covalent reactions can be carried out on such frameworks, with full retention of their crystallinity and porosity. MOFs are exemplars of how this chemistry has led to porosity with designed metrics and functionality, chemically-rich sequences of information within their frameworks, and well-defined mesoscopic constructs in which nanoMOFs enclose inorganic nanocrystals and give them new levels of spatial definition, stability, and functionality. The advent of COFs extends the field of organic chemistry beyond discrete molecules (0D) and polymers (1D) into “infinite” two and three dimensions. Molecular weaving, the mutual interlacing of long threads at the molecular level, was first accomplished in COF to make the true woven material. This discovery combines the porosity and robustness of frameworks with mechanically deformable and stretchable capability.

Sir James Fraser Stoddart of the Department of Chemistry, Northwestern University, lectured on “Materials Beyond Cyclodextrins Emergence Opens Up a Whole New World of Wonders.” He explained that during the past decade members of his research group have made two momentous discoveries in the area of carbohydrate materials, each having the potential to become a ‘disruptive technology’ for environmentally friendly products and sustainable processes. The two materials, both of which incorporate cyclic sugars known as cyclodextrins (CDs), are readily available from starch and are inexpensive and environmentally benign. Promising as these

materials are for technologies ranging from food processing to gold mining, they also constitute exquisite examples of molecular self-assembly processes, aided and abetted by molecular recognition where: (i) the four-fold γ -CD molecular symmetry with eight glucose units orchestrates the spontaneous formation of the first edible metal-organic frameworks (MOFs) containing alkali metal (M^+) cations, and (ii) the selective second-sphere coordination of potassium tetrabromaurate ($KAuBr_4$) by α -CD, with its six glucose units, leads to the selective bulk separation of the gold salt by precipitation, even in the presence of other precious metals. The secret behind the CD-MOF formation is the simultaneous coordination of M^+ ions to both primary and secondary γ -CD toroidal faces, promoting the assembly of $(\gamma\text{-CD})_6$ cubes linked in an infinite 3D network. Crystallization under mild conditions yields CD-MOF cubes having dimensions of up to 5 μm , where the extended molecular structures are retained, even upon evacuation, to yield a highly porous material capable of accommodating small molecules in its pores. In the case of CO_2 , highly selective uptake is shown to involve reversible formation of carbonic acid under Le Chatelier-like control at 25 °C. The same CD-MOFs also serve as chiral stationary phases for the chromatographic separation of flavors and fragrances, as well as separating aromatic compounds such as xylene isomeric mixtures. Initially following the discovery of CD-MOFs, his group assumed that the nature of the anion accompanying the M^+ cations was of little or no significance. However, they discovered that when the anion is $AuBr_4^-$, a 3D channel-like superstructure results, wherein the gold-containing anions are interspersed along the CD units. The key enabling discovery came when they observed that, when dilute aqueous solutions of $AuBr_4^-$ and α -CD are mixed under ambient conditions, an off-white precipitate forms in near-quantitative yield. X-Ray diffraction characterization of the resulting complex, $\{[K(OH)_2][AuBr_4]/(\alpha\text{-CD})_2\}$, revealed a superstructure embodying a perfect lock-and-key component match that drives the precipitation of the gold-bearing adduct. Transmission electron microscopy showed that the precipitate is composed of high-aspect ratio nanowires having lengths in the tens of micrometers range. This discovery heralds a potential game-changer for recovering elemental gold from ores to electronic waste. The gold isolation process is simple, selective, scalable, and cost-efficient. The only requirement prior to the addition of α -CD is that the gold-bearing materials be dissolved in aqueous KBr and Br_2 solutions which are relatively safe to handle unlike the current cyanide-based leaching process used in 83% of the world’s gold production.

Kimoon Kim of the Center for Self-Assembly and Complexity, Institute for Basic Science and Department of Chemistry, Pohang University of Science and Technology, Pohang, Korea, lectured on “Nanostructured materials by covalent self-assembly.” He explained that one of the most exciting developments in chemistry during the last two decades has been the construction of nanostructured objects or materials from small building blocks by self-assembly. However, most of these studies utilize weak noncovalent

interactions between building blocks, which allow a reversible process ultimately leading to the formation of thermodynamically most stable species. Some years ago, his group reported the direct synthesis of nanometer-sized polymer hollow spheres without need for any pre-organized structures or templates, and core-removal. In this work, flat and rigid-core tectons with multiple functional groups isotropically predisposed in all directions were cross-linked with linear linkers through irreversible covalent bond formation. These polymer capsules are useful in many applications, including targeted drug delivery, photodynamic therapy, catalysis, and imaging. Extending this work, they also demonstrated the synthesis and isolation of micrometer-scale 2D polymer sheets of single-molecular thickness, which may find interesting applications including separation, optoelectronics and sensor. This strategy has also been extended to synthesize other nanostructured materials including hollow nanotubular toroidal polymer micro rings. These are rare examples of covalent self-assembly under kinetic control, and recent progress was partially covered by this lecture.

Meir Lahav of the Weizmann Institute of Science, lectured on “Understanding Electrofreezing at the Molecular Level with Pyroelectric Crystals.” This work was carried out in collaboration with D. Ehre, S. Curland, E. Meirzadeh, I. Lubomirsky of the Weizmann Institute, and Ch. Allolio and D. Harris of the Hebrew University of Jerusalem. Lahav explained that pyroelectric crystals are useful systems for the elucidation of structures and functions of materials. He illustrated their use for the determination of the mechanism of electrofreezing on the molecular level. Electrofreezing of super-cooled water, discovered at the 19th century is of topical importance in the pure and applied sciences. Yet, the mechanism of this process at the molecular level remains unsettled. In early studies this group reported that polar pyroelectric crystals induce ice nucleation at temperatures higher by 3–5 °C in comparison to icing induced by analogous non-polar materials. More recently, by the application of polar crystals, they discovered that the temperature of super cooled water is augmented on positively charged surfaces, whereas reduced on negatively charged ones. Consequently, they observed the occurrence of pyroelectric currents, which flow on hydrophilic faces residing parallel to the polar axes of the amino acids L-cysteine, DL-alanine, L-aspartic acid, D-4-hydroxyphenylglycine and LiTaO₃. This pyroelectric current can be cancelled when linking the hemihedral faces of those crystals with a metallic conductive paint. However, no such currents are observed on analogous hydrophobic surfaces. Hence, by comparing the icing temperatures, measured exactly on the same surface in the presence and the absence of the electric current, the effect of the pyroelectric charges on the icing temperature could be isolated from other factors. These studies suggested that the charges responsible for ice nucleation are OH⁻ ions, which migrate towards and consequently incorporate within the aqueous Debye layers residing near the positive charged surfaces. Subsequently, proton ordered ice-like nuclei of the required size, as needed

for triggering the icing, are created. These results were supported by molecular dynamics simulations, which suggest that electrofreezing is a chemical process affected by OH⁻ ions. Moreover, in recent studies they demonstrated that the pyroelectric effect operates also in the icing on AgI, used for the glaciation of warm clouds.

Lars Öhrström of the Department of Chemistry and Chemical Engineering Chalmers University of Technology at Gothenburg, Sweden, lectured on “Designing, Describing and Disseminating New Materials using the Network Topology Approach.” He described how network topology analysis is applied to different fields of solid-state chemistry, including Metal-Organic Frameworks (MOFs), group 14 allotropes and related compounds, ice polymorphs, zeolites, supramolecular (organic) solid-state chemistry, Zintl phases, and cathode materials for Li-ion batteries. Recent IUPAC recommendations and ongoing work on the terminology and nomenclature of MOFs was also discussed. Finally, he mentioned how metal-organic frameworks challenge our perceptions about the properties of crystalline materials.

Laura Gagliardi of the Department of Chemistry, Chemical Theory Center, and Supercomputing Institute, University of Minnesota, Minneapolis, lectured on “Computational Design of Functionalized Metal-Organic Framework Nodes for Catalysis.” She explained that metal-organic frameworks (MOFs) are attracting the attention of many scientists because of their high selectivity in gas separations, catalytic activity, and magnetic properties. Her group has combined theory and experiment to understand the activity of metal catalysts supported on Zr₆ nodes in metal-organic frameworks (MOFs) for reactions related to natural gas conversion, like catalytic oligomerization of abundant C₁, C₂, and C₃ hydrocarbons to longer congeners or selective oxidation to alcohols or other fuel molecules, while avoiding overoxidation to water and carbon dioxide. For Ni and Co, computational studies provide important insights with respect to the catalytic mechanism(s) for observed ethylene dimerization after metal-decoration of the MOF NU-1000. Rh complexes have been installed on the Zr₆ nodes of not only NU-1000, but also the related metal-organic framework UiO-67, and the zeolite DAY; influences of the supports on ethylene hydrogenation and dimerization have been assessed. A library of transition metals (TMs), ranging from first row TMs to noble metals, is now being screened computationally to search for optimal catalysts, and structure-function relationships are beginning to emerge from this theory-driven approach.

Yoram Cohen of the School of Chemistry, The Sackler Faculty of Exact Sciences, and the Sagol School of Neuroscience, Tel Aviv University, lectured on “Diffusion NMR in Supramolecular Systems and Beyond.” He pointed out that diffusion NMR and diffusion ordered spectroscopy (DOSY) have developed into an important analytical tool which can assist in the characterization of supramolecular systems in solution. In his lecture, after a brief introduction of the technique, he presented the contribution of diffusion NMR to the field of molecular cages and capsules concentrating more

on hydrogen bond-based molecular capsules. The use of diffusion NMR in studying self-assembled polymers was mentioned briefly. He demonstrated the effect that exchange may have on the diffusion NMR results when diffusion is measured using the longitudinal eddy current delay (LED)-based sequences generally used in DOSY. Finally, he introduced the angular double pulsed-field gradient (d-PFG) NMR sequence and demonstrated how this sequence provides a mean to obtain microstructural information in dense micro-emulsions, plants and neuronal tissues.

Qing-Fu Sun of the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, was scheduled to lecture on “Lanthanide Organic Polyhedra.” He planned to describe his work on designed self-assembly and fine-tuned photophysical properties of multinuclear lanthanide-organic polyhedral (LOPs) complexes. In particular, he intended to discuss the chiroptical properties of the LOPs with proof-of-concept applications, such as highly selective sensing of biologically relevant molecules and ions, ion separation, single-molecular radiometric luminescent thermometers and photosensitizers. Unfortunately, he was unable to attend the symposium due to unexpected circumstances in China.

Tomohisa Sawada of the Graduate School of Engineering, The University of Tokyo, lectured on “Concerted folding-and-assembly of short peptides via coordination.” He explained that folding and assembly are respectively intra- and inter-molecular processes for spontaneously generating well-defined protein structures in natural systems. However, in synthetic fields, such processes have been utilized independently for constructions of well-defined nanostructures to date. Recently, his research group have developed the folding-and-assembly strategy, in which short peptide fragments can self-assemble into a well-defined nanostructure through concerted processes of folding and assembly triggered by metal coordination. He proposed that this new synthetic strategy is especially useful for creating unique nanostructures with multiple peptide entanglements. In his presentation, a variety of unique nanostructures such as porous coordination networks composed of polyproline II helices, interlocking molecules based on Ω -shaped loops, and others, were reported.

Milko van der Boom of the Department of Organic Chemistry, Weizmann Institute of Science, lectured on “Made in Israel: Metallo-Organic Materials and Devices.” He explained that electrochromic coatings change color as a function of an applied potential. This interesting property is useful for various applications, including smart windows, color displays, and sensors. Fabricating low-cost electrochromic coatings that have appealing colors, and large optical contrasts, as well as long-term stability, remains an engineering challenge. Organic polymers, metal oxides, and liquid crystals have been promising candidates. He described molecular materials developed in his group, which are based on structurally well-defined metal complexes that can be deposited from solution, offer a wide range of colors, and have metal-centered stable and reversible redox chemistry.

Xiaoyu Cao of the College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China, lectured on “Molecular Face-Rotating Polyhedra.” He explained that in nature, protein subunits on the capsids of many icosahedral viruses form rotational patterns, and mathematicians also incorporate asymmetric patterns into faces of polyhedra. His group used prochiral truxene or tetraphenylethylene derivatives as building blocks to construct a series of molecular polyhedra with rotational patterns on faces, which we term as Face-Rotating Polyhedra (FRP). The relative stability of these polyhedra enables separation by chiral HPLC and full characterization. They investigate the assembly process and the kinetics of interconversion of the polyhedra by a combination of chiral HPLC, CD, MS and NMR. These FRP represent a special form of molecular chirality.

Takuzo Aida of the Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, and Riken Center for Emergent Matter Science at Saitama, Japan, delivered the final lecture on “Smart Soft Materials Fabricated under Non-equilibrated Conditions.” He explained that machine technology frequently puts magnetic or electrostatic repulsive forces to practical use, as in maglev trains, vehicle suspensions or non-contact bearings. In contrast, materials design overwhelmingly focuses on attractive interactions, such as in the many advanced polymer-based composites, where inorganic fillers interact with a polymer matrix to improve mechanical properties. However, articular cartilage strikingly illustrates how electrostatic repulsion can be harnessed to achieve unparalleled functional efficiency: it permits virtually frictionless mechanical motion within joints, even under high compression. In his lecture he described a composite hydrogel with anisotropic mechanical properties dominated by electrostatic repulsion between negatively charged unilamellar titanate nanosheets embedded within it. Crucial to the behaviour of this hydrogel is the serendipitous discovery of cofacial nanosheet alignment in aqueous colloidal dispersions subjected to a strong magnetic field, which maximizes electrostatic repulsion and thereby induces a quasi-crystalline structural ordering over macroscopic length scales and with uniformly large face-to-face nanosheet separation. His group fixes this transiently induced structural order by transforming the dispersion into a hydrogel using light-triggered in situ vinyl polymerization. The resultant hydrogel, containing charged inorganic structures that align cofacially in a magnetic flux, deforms easily under shear forces applied parallel to the embedded nanosheets yet resists compressive forces applied orthogonally. Aida anticipated that the concept of embedding anisotropic repulsive electrostatics within a composite material, inspired by articular cartilage will open up new possibilities for developing soft materials with unusual functions. More recently, his group reported a highly oriented thin film of a carbon nitride polymer, which shows anomalous mechanical responses to minute fluctuations in the ambient humidity. The lecture also highlighted their recently published self-healable polymeric glass.

Concluding Remarks

Ehud Keinan made a few comments at the end of the scientific program. “It has been a fabulous day, I’ve enjoyed every single lecture and many people in the audience shared with me similar opinions the same feelings. It was an appropriate prelude for the Wolf Prize ceremony, which will take place tomorrow evening in the Knesset. I think I have attended all Wolf Prize ceremonies over the past 30 years, but every year I experience excitement and emotions, up to the level of tears in my eyes, as if it was the first time. I wish to conclude this symposium by making two points, which came up repeatedly during the day.

The first point is about the special nature and essence of the Wolf and Nobel prizes which make them unique. Most prizes around the world highlight an outstanding scientific career. However, the Wolf and the Nobel focus on a specific conceptual advance. The committees select the most significant conceptual advance in the given field and then select the pioneers who deserve the credit for the original concept. Consequently, these prizes are not only about science, but also about the history of science. Thus, in many past cases we have seen laureates who were not necessarily contributing more than others, but those who were identified as the actual pioneers. I think that the laureates of the 2018 chemistry prize are not only the pioneers, but also those who have made the most significant contributions to their fields.

The second point I wish to make is about the inspiration we get from other fields, particularly from biology, and we are familiar with many terms, such as *biomimetic*, *bioinspired engineering*, etc. We do not mimic Nature in the straightforward manner. The only lesson we take from Nature is that a certain device or a certain principle can be realized using molecules. For example, Boeing 777 does not fly by flipping its wings like a bird. The major concept that aerospace

engineers have borrowed from Nature is that heavier-than-air machines can fly. The actual realization of such machines utilizes concepts of mechanical engineering, chemistry, physics and materials science, certainly not biology. The same is true for molecular motors. All that we’ve learnt from watching the bacterial flagellar movement and ATPase is that creating molecular motors is possible, but the actual technology used by Nature is not the one chosen by Jean-Pierre Sauvage, Fraser Stoddart and Ben Feringa to create their devices.

Finally, I’d like to sincerely thank all speakers, and chairpersons (Figure 5), and the audience. I know that most speakers travelled a long distance to attend this event and we all deeply appreciate your efforts. Finally, I wish to thank the sponsors, including the Technion, the Schulich Faculty of Chemistry, the Berkeley Global Science Institute, Rigaku Corporation of Japan, Tokyo Chemical Industry (TCI) Co., and Merck Sharp & Dohme (MSD) Corporation. I am grateful to our Project Manager Liraz Maanit, and the people of the Wolf Foundation and the Schulich Faculty of Chemistry. Thanks to the dedicated people in the audience. I hope to see you again next year in the Wolf Symposium of 2019.”

Wolf Prize Ceremony, the Knesset, May 31, 2018

The Wolf Prize, nicknamed ‘Israel’s Nobel Prize’, is considered by many as a strong predictor of the Nobel, since approximately one third of Wolf laureates were subsequently awarded a Nobel Prize. Since 1978, five or six prizes have been awarded annually in the fields of agriculture, chemistry, mathematics, medicine and physics, whereas the arts prize rotates annually among architecture, music, painting and sculpture. The prize in each field consists of a certificate and a monetary award of \$100,000, which can be shared by two or



Figure 5. Group photo of all lecturers and chairpersons. From left: Sharon Ruthstein, Maya Bar Sadan, Lars Öhrström, Kimoon Kim, Omar M. Yaghi, Sir J. Fraser Stoddart, Ehud Keinan, Laura Gagliardi, Makoto Fujita, Milko E. van der Boom, Takuzo Aida, Xiao-Yu Cao, Tomohisa Sawada, Galia Maayan and Meir Lahav.

three recipients. Award winners are selected by international awards committees consisting of three members; all of whom are scholars and experts in their fields. Each committee is appointed for one year. The deliberations and recommendations of the committees are kept strictly secret, and only the names of the winners and the reasons for the decision are published. The committees' decisions are final and cannot be appealed. To date, 329 recipients have been selected from 23 countries to receive the prize from the President of the State of Israel.

The Wolf Foundation began its activities in 1976, with an initial endowment fund donated by the Wolf family. The Foundation's founders and major donors were Dr. Ricardo Subirana y Lobo Wolf and his wife Francisca. Annual income from investments is used for prizes, scholarships and Foundation operating expenses. The Foundation holds the status of a private not-for-profit organization. Its objectives and prize administration details and procedures are grounded in the "Wolf Foundation Law-1975". Israel's State Comptroller oversees all of the Foundation's activities. In accordance with the above-mentioned Law, the Minister of Education acts as Chairman of the Council. Foundation Trustees, Council and Committee Members, Prize Juries, and Internal Auditor all perform their duties on a voluntary basis. The fund targets as set out in the law are: "promote science and art for the benefit of humanity. Grant awards to scientists and artists renowned for their achievements for mankind and friendly relations among peoples, irrespective of nationality, race, color, religion, sex or political view."

The ceremony has always taken place in the Chagall State Hall of the Knesset Building (Israel's Parliament), in Jerusalem. This is the 40th year of awarding the Wolf Prizes. The Jewish artist Marc Chagall (1887–1985) designed and decorated the hall and its 12 floor mosaics, one wall mosaic and three Gobelin tapestries. The tapestries were ordered in 1965 and were produced over a period of four years. The work is presented in the form of a triptych in which each of the parts is both part of the whole and a separate unit. They represent a sort of concise and poetic expression to the fatefulness of the Jewish people.

The prizes were awarded by President of the State of Israel, Mr. Reuven (Ruvi) Rivlin; Minister of Education and Chairman of the Wolf Council Naftali Bennett; Knesset deputy speaker, MK Nachman Shai; Acting Chairperson of the Wolf Council, Prof. Dan Shechtman; and CEO of the Wolf Foundation, Ms. Reut Inon Berman. Seven scientists and one artist received the 2018 Wolf Prizes (Figure 6).

The Wolf Prize for Agriculture was awarded to **Prof. Gene Robinson** of the University of Illinois, Urbana-Champaign, for leading the genomics revolution in organismal and population biology of the honeybee.

The Wolf Prize for Physics was shared by two laureates: **Dr. Charles H. Bennett** from IBM Research Center, Yorktown Heights, NY, USA, and **Prof. Gilles Brassard** from the University of Montréal, Canada, for founding and advancing

the fields of Quantum Cryptography and Quantum Teleportation.

The Wolf Prize for Mathematics was shared by two laureates: **Prof. Alexander Beilinson** and **Prof. Vladimir Drinfeld**, both from the University of Chicago, for their groundbreaking work in algebraic geometry, representation theory, and mathematical physics.

The Wolf Prize for Music was awarded to **Adam Fischer**, an inspirational conductor and eloquent defender of human rights.

The Wolf Prize for Chemistry was shared by two laureates: **Prof. Makoto Fujita** of the University of Tokyo, for conceiving metal-directed assembly principles leading to large, highly porous complexes, and **Prof. Omar Yaghi** of the University of California at Berkeley, for pioneering reticular chemistry via metal-organic frameworks and covalent organic framework.

Detailed Justifications for the Prize to Prof. Makoto Fujita

Traditional chemistry has focused on intermolecular connections, particularly on strong covalent bonds formed when two atoms share one or more electrons. In contrast, supramolecular chemistry deals with the study of connections and interactions between molecules – a study that promotes the development of novel materials with unique properties that are sometimes very useful.

Makoto Fujita, born in 1957, developed his academic career quickly and at the age of 42 was appointed full professor at Nagoya University. Three years later (2002) he was appointed to the same position at Tokyo University, the most prestigious university in Japan. He was soon recognized as one of the pioneers in the field of supramolecular chemistry and was awarded many prizes: the Arthur C. Cope Scholar Award from the American Society of Chemistry, the Izatt-Christensen International Award for Macrocyclic Chemistry, the International Society for Nanoscale Science, Computation, and Engineering (ISNSCE) Award, The Fred Basolo Medal for Outstanding Research in Inorganic Chemistry from Northwestern University and the Nagoya silver medal. Fujita's impressive academic yield, since the beginning of his academic career till today (i.e., between 1980 and 2017), includes approximately 330 publications.

Makoto Fujita's main contribution to Supramolecular Chemistry has been the development of a new method for the formation of supramolecular structures called "metal-guided synthesis" or "self-assembly with metallic guidance". This novel method enables quick and spontaneous assembly (under specific thermodynamic conditions) of supramolecular materials, and is much easier and more effective than the cumbersome, tedious, and highly inefficient methods previously used to synthesize such materials. As early as 1990, Fujita published an article describing this method of synthesiz-



Figure 6. Collage of photos from the Wolf Prize ceremony in the Knesset on May 31, 2018. Photos by the Wolf Foundation.

ing materials on a nanometric scale containing both metal ions and various organic molecules (i.e., molecules containing carbon and hydrogen atoms connected to each other). In the

years that followed, this method was used to build increasingly complex molecules, nanostructures and materials. Fujita's group, for example, synthesized three-dimensional porous

molecules, called “cages”, that can be used as molecular “containers” that store smaller molecules. This structure may give the trapped materials new chemical properties; for instance, it may increase the solubility of drugs and therefore their effectiveness.

Several years ago, Fujita and his colleagues managed to synthesize a cage large enough to store protein molecules in its pores. This is of great practical importance since many new drugs are protein-based. In 2016, they succeeded in assembling a relatively large cage, 8 nanometers wide, and later that year they theoretically proved that with the self-assembly method they had developed, it is possible to assemble 144 such cages into one stable, giant cage. A particularly important and interesting application of these large cages, developed by Fujita himself, is the possibility of using them for x-ray crystallography (for studying the crystalline structure of matter) without even having to produce a crystal of the material being tested. Instead of this, the material can be “imprisoned” in a synthesized cage that positions and stabilizes it in such a way that it can be directly examined using standard crystallography.

Response of Prof. Makoto Fujita

“Thank you very much. This is really a great honor for me to receive the Wolf Prize in Chemistry. First of all, I am very appreciative for the recognition of our chemistry by the Wolf Foundation and for arranging this wonderful event. This reminds me of the very early stages of my scientific career. In the summer of 1990 we noticed the chemical principles of the metal-directed self-assembly which eventually led to the current recognition of our work.

At the same time, in the summer of 1990, our daughter was born. So, both my chemistry and my daughter are exactly of the same age, and I have been watching their growth. At the beginning, when both were babies, every day they brought me new discoveries, new excitements and happiness. Very often I was surprised by their very fast growth, and occasionally I found them difficult to control... Now they have both grown up, they go around the world, having their independent life.

I would like to take this opportunity to thank my many coworkers and, in particular, my family. Without their support, continuous encouragement and contribution, I would never be able to come to this event today. Thank you very much.”

Detailed justifications for the prize to Prof. Omar M. Yaghi

Traditional chemistry has focused on intermolecular connections, particularly on strong covalent bonds formed when two atoms share one or more electrons. In contrast, supramolecular chemistry deals with the study of the connections and the interactions between molecules – a study that promotes the

development of novel materials with unique properties that are sometimes very useful.

Omar Yaghi of the University of California at Berkeley, born in Amman in Jordan (1965), is a member of a refugee family with many children. At the age of 15 he was sent to the United States and soon became prominent for his outstanding talent for science. In 1985, Yaghi began his doctoral studies in chemistry at the University of Illinois at Urbana-Champaign. After completing his studies, he completed a post-doctorate at Harvard. In 1992, he gained his first independent academic post at the Arizona State University. This is where he actually conceived, developed, and finally began to apply his grand, chemical program to bond molecules together – through strong bonds – to large “frameworks”. His achievements in this field have earned him many awards, including the Sacconi Medal of the Italian Chemical Society, the Izatt-Christensen International Award, the Materials Research Society Medal, the King Faisal International Prize in Science (also known as the Arab Nobel Prize), the Mustafa Prize in Nano-Science and Nano-technology and the Albert Einstein World Award of Science conferred by the World Cultural Council.

Yaghi is actually the main developer of a new branch in supramolecular chemistry called “Reticular Chemistry” (In Latin “reticulum” means “small grid”). Reticular Chemistry makes it possible to combine molecules into networks that create highly porous structures with a very large surface area, enabling the efficient storage and handling of various materials “trapped” in pores (for example, various gaseous fuels), and efficient capture and storage of elements and compounds such as carbon and water. The porous feature is very important for practical purposes, as it enables the capture and compact storage of large quantities of gases in small volumes.

Through the use of Reticular Chemistry, Yaghi developed two entirely new types of compounds, called metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). While the supramolecular chemistry was initially limited to relatively weak bonds, such as hydrogen bonds and Van der Waals interactions, the great advantage of Reticular Chemistry is its success in creating supramolecular structures, frameworks with very strong, covalent bonds between molecules that give them unprecedented chemical and structural strength. Thanks to Reticular Chemistry each of these frameworks can be viewed as a molecule. Just as the molecule determines the specific geometry and spatial array of each of the atoms, so too does the framework determine each of the molecules in a well-defined geometry and well-defined spatial array. Actually, in view of the fact that these frames encompass relatively large volumes, their chemistry is much richer than that of the molecules of which they are comprised, enabling them to impart unique properties. There are many possible applications for this. For example, producing materials that capture carbon dioxide very efficiently may reduce the rate of gas entering the atmosphere, thereby reducing the trend of global warming.

Response of Prof. Omar M. Yaghi

“Your Excellency President Reuven Rivlin, Friends and Colleagues, Ladies and Gentlemen, Greetings from the heart: Hello, Shalom, Salam.

I want to thank the Wolf Foundation (officers and staff) and the selection committee members for their work and for honoring me with the 2018 Wolf Prize in Chemistry. What a brilliant decision to share the prize with Professor Makoto Fujita. I value and appreciate those who wrote on my behalf and nominated me for the prize, for their confidence in me.

I was born and raised in Amman, Jordan. My family originally comes from a village not far from here – making this occasion moving to me and I detect to some of you as well. I like to say that scientific discovery is a gift to humanity. It transforms our world for the better, while profoundly transforming us as human beings, and indeed our understanding of each other and the world. I speak of science as the language of peace where scientific discovery is its currency.

My love for chemistry started at an early age when I saw drawings of what I later learned to be molecules. They appeared simple and mysterious and to me they were beautiful. Little did I know that one day I would be the one to stitch and weave these together to make intricate structures and materials with myriad of uses such as harvesting water from desert air and capturing carbon dioxide. Our discoveries gave rise to a new field we call reticular chemistry, which is being practiced worldwide. It is the thrill of my life. It is my life!

Although, I had what one would call a less easy life, both as a child living in humble conditions and as an adult who bucked the trends in chemistry, I have always been fortunate to be heard through my work and to have the support of others. Yes, I am blessed! There is no doubt in my mind that my Muslim upbringing and the work ethic values my parents instilled in me and the independence they gave me as a child helped me in navigating life's challenges. These values encouraged commitment to excellence in one's work; they urged freeing of one's mind to learn and see clearly ahead; and they recognized the transformative impact of listening to critique no matter how difficult that might be.

I would like to thank my doctorate advisor (Walter G. Klemperer) who taught me that ‘science begins with doubt and questions’ and my postdoctoral advisor (Richard H. Holm) who taught me that ‘science is an exercise in optimism’. They mentored me and gave their time selflessly and unconditionally. There are also individuals we meet along our life's journey whose kindness gives us faith in humanity because they volunteer their time and support and believe in us. Sir J. Fraser Stoddart, who is present here tonight, is one such person. Also, the late Dr. Ron Allain, an industrialist, who compelled me to take my basic science all the way to address societal challenges. I want to also express my appreciation to the sea of colleagues and friends all over the world (including those present here tonight) who expressed their warm congratulations. I want to say to my former students and current research group members who, in their research, ‘fail, fail and fail’ so that they may succeed: I admire you and you inspire me every day.

To continue the passing of mentorship from one generation to the next so that we may continue to make scientific discoveries, I wish to announce here tonight my intent to donate my prize funds for scholarships to help students who have hopes, dreams, and the will to improve, but do not have the opportunity. The funds will be a seed in a larger and a far-reaching effort designed to help young scholars from this region, regardless of their religion, gender, and national origin, to explore, to discover, to build their lives, and to be forces of good in the world. Let this be the first step upon which we can build together so that the human spirit endures regardless of prevailing circumstances. Thank you very much.”

References

- [1] E. Keinan, *Israel. J. Chem.* **2017**, *57*, 171–352.
- [2] E. Keinan, *Israel. J. Chem.* **2017**, *57*, 1053–1066.

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CONFERENCE REPORT



*E. Keinan**

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**Metal-Directed Assembly and
Metal-Organic Frameworks: ICS
Symposium Honoring Wolf Prize
Laureates Makoto Fujita and
Omar M. Yaghi, May 30, 2018,
Technion – Israel Institute of Tech-
nology, Haifa, Israel**
