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Reticular Chemistry: Special Issue in Honor of the 2018 Wolf Prize Laureate in Chemistry, Professor Omar Yaghi

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In 1976, the inventor Dr. Ricardo Subirana y Lobo Wolf and his wife Francisca created the Wolf Foundation to highlight *"achievements in the interest of mankind and friendly relations among people"* in Sciences and Arts. Two years later the Wolf Prizes were established and since then, the Wolf Prize in Chemistry has been considered one of the most prestigious scientific awards in the world.

This year, the Wolf Prize in Chemistry recognized two high impact developments in chemistry. Prof. Makoto Fujita was honored *"for conceiving metal-directed assembly principles leading to large highly porous complexes*," and Prof. Omar M. Yaghi was honored "*for pioneering reticular chemistry via metal-organic frameworks (MOFs) and covalent organic frameworks (COFs)*." Prof. Omar M. Yaghi is the James and Neeltje Tretter Chair Professor of Chemistry at the University of California, Berkeley.

The ceremony was hosted by the President of Israel, who made an additional and special reference when announcing the award to "Professor Omar Yaghi, a native of Amman in neighboring Jordan – together prove that the human spirit has no limits and no borders when it works for humanity".

A few days after the prize was announced, Prof. Ehud Keinan, President of the Israel Chemical Society and Editor-in-Chief of the *Israel Journal of Chemistry* invited us to serve as Guest Editors for a special issue of the journal on Reticular Chemistry, honoring Prof. Omar Yaghi. We were honored to accept the invitation and thereby join the recognition of Prof. Yaghi as the pioneer in the field. It has been a gratifying pleasure designing, inviting contributors and reviewers, supervising the whole process, and finally, offering this special issue to the scientific community. This issue recognizes Prof. Yaghi's groundbreaking scientific achievements, and what is also important to us, his sincere friendship.

Reticular Chemistry has led to a plethora of scientific contributions and to applications that will help make a better world. In Omar Yaghi's words "Reticular Chemistry, the chemistry of linking molecular building blocks by strong bonds to make crystalline open frameworks, has significantly expanded the scope of chemical compounds and useful materials. Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) exemplify the manner in which this chemistry is practiced and epitomize the molecular-level control being exercised over matter".[1]

No doubt, MOFs represent the class of chemical compounds that have had the greatest growth in the history of chemistry. Since the 90′s more than 60,000 varieties of developed MOFs have been reported due to the practically infinite number of possible new or modified frameworks and their remarkable new and numerous applications: gas, liquid, and vapours storage and separation, including enantioselective abilities; catalysis including chiral catalysis; chemical sensing; ionic and electronic conductivity, and many more. It's worth highlighting here the new application for harvesting atmospheric water in desert environments with MOFs that was pioneered by Yaghi and his group.[2] The method allows for collecting 200 ml of water/day/kg of MOF with no energy input other than that of ambient sunlight.

New COF compounds are being developed, but with much lower rates in terms of new materials. This is reasonable if we consider that the equilibrium of the reactions carried out to form COFs are typically strongly shifted to the right, hindering the crystallization defects self-correction and frequently resulting in amorphous organic polymers. Once again, Omar Yaghi and collaborators have opened a new window by describing a synthesis methodology to grow "giant" (1/10 millimeter) single crystals of COFs.[3]

Such a large number of new frameworks requires a rational topologic study of their new structures defining nodes, rings, nets and tiles to develop unified nomenclature and deposit all new topologies in dedicated open databases (i.e. Reticular Chemistry Structure Resource, RCSR[4]). In addition, frameworks can be composed of more than one net, giving rise to interpenetrated, polycatenated or interweaving nets, which impact the material properties. Nowadays, having such a level of complexity is an important tool to rationally design new open frameworks with specifically targeted properties.

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Several moments during the 2018 Wolf Prize award ceremony hosted by the President of the State of Israel, Mr. Reuven Rivlin (courtesy of the Wolf Foundation).

This special double issue includes excellent contributions submitted by renowned researchers in the field of Reticular Chemistry including Yaghi's former students, collaborators, and colleagues who were enthusiastically willing to contribute reviews, original research articles, and communications.

The topics cover a wide scope of Reticular Chemistry ranging from applied mathematics and net topology, to new properties and applications of MOFs and COFs, passing through multi-metal synthesis, and depicting how the guest molecules interact inside the porous structure or the electronic transport along the structure in conducting MOFs. New structures and topologies, post-synthetic modifications, catalysis, polymerization, storage and gas separation experiments are carefully described, as well as the new possibilities that electron microscopy in combination with X-ray diffraction offer to the study of less crystalline MOFs and COFs.

Liu and O'Keefe provide a comprehensive review beginning with the description of the topological bases (nodes, rings, nets, tiles) to interpenetrated, polycatenated and interwoven nets. They have provided multiple examples showing how to deconstruct some complex nets of MOFs and COFs. It is a particularly valuable contribution for beginners in the field.

Thompson and Hyde theoretically explore weaving on the sphere, the Euclidean plane, and the hyperbolic plane and conclude by visiting the still few cases of known interwoven networks of MOFs and COFs.

Banglin Chen *et al.* review the applications of MOF in regard to two of the most important characteristics: permanent porosity and the large internal surface. They also summarize their progress in gas storage, gas separation, optical response, chemical sensing, proton conduction, and molecular recognitions.

The contribution made by Zhao-Liu Shi and Yue-Biao Zhang focuses on reviewing methane storage capacities of MOFs from initial studies to present, showing how MOFs with ultra-high porosity are surpassing the U.S. Department of Energy target to on-board methane storage applications.

Felipe Gándara and Celia Castillo provide an overview on the formation of multi-metal MOFs, and show how the ability to create new chemical environments by placing together multiple metal elements opens up new opportunities to finely modulate the properties of these materials.

Richard Walton and Franck Millange emphasize the crystal chemistry of the abundant MIL-53 type structure MOFs, and provide some examples of their properties, particularly those associated with the structural breathing effect of relevance to molecular sieving.

Jorge A. R. Navarro reviews the influence of defects on pyrazolate based metal organic frameworks.

Jaheon Kim and collaborators analyze the relationship between the chemical compositions and the three-dimensional structures and topological properties of all known zeolitic imidazolate frameworks (ZIFs) to date. They explain the connectivity patterns of the inorganic and organic building components in each type of nets.

Seth Cohen and co-workers explore the possibility of preparing poly-MOFs using *ortho*-substituted benzene dicarboxylate polymer linkers with different length alkyl spacer and compare the changes when they use the corresponding *para*-substituted linkers.

Lars Öhrström *et al.* present two new coordination compounds with potential porosity; one presents a new topology and the other exhibits a tetranuclear secondary building unit (SBU), which could lead to new MOFs.

Alessia Bacchi *et al.*, based on careful structural analyses by single crystal X-ray diffraction, have studied the interaction between solvent molecules and open metal sites containing MOFs. IRMOF-9 *drink* and *breath* solvent molecules establishing that strong coordination bonds with the metal atoms trigger dramatic coordination changes on the SBU and structure of the MOF.

Alejandro Fracaroli and Rita H. de Rossi report different approaches to add supramolecular chemistry features into the MOF by incorporating macrocycles into the pores of MOFs, combining the selectivity, coming from the periodic open structures of the MOFs, with the well-known molecular recognition capacities of the macrocycles.

Jeffrey R. Long and collaborators detail the investigation of Co_2(m-dobdc) and Ni_2(m-dobdc) as selective adsorbents for Xe over Kr, demonstrating key differences in the binding of Xe and Kr within the materials through in situ Xe- and Kr-dosed powder X-ray diffraction studies.

Maria Celeste Bernini *et al.* revise the literature on rare-earth succinate frameworks with potential catalytic and photoluminescent applications.

Avelino Corma and Pilar García summarize the catalytic applications of Hf-MOFs since their initial development in 2012, according to the location of the active site. Special emphasis is placed on synthetic preparation and the particular feature of these materials that allow to exert local defects engineering in the MOF structure, which influence remarkably on the reactivity, while maintaining the stability and the global crystallinity.

Tasaki Uemura and Benjamin Le Quay review the reactions of polymerization inside MOF pores including those that take place when guest molecules (monomers) interact strongly with each other inside the porous MOF structures, forming covalent bonds and giving rise to polymers with special characteristics inside MOF structures. These new compounds are composites with new properties, and the confinement influence is even preserved after a controlled decomposition of the MOF template resulting in long range ordered polymers with a kind of memory of the channeled structure of the sacrificial MOF.

Bo Wang and Pengfei Li's interesting review of the development and application of conductive MOFs provides great interest for chemists, physicists, and engineers studying device fabrication and design.

Thomas Bein, Dana D. Medina and Andre Mähringer review the concepts of reticular chemistry, and focus to the structural features of the 2D and 3D MOFs, to link them to the prominent examples reported for electrically conducting MOFs with regard to their synthesis, structural and electronic properties, and possible applications.

Mircea Dincă and Lilia S. Xie report new MOFs of the three smallest lanthanide ions (Tm3 +, Yb3 +, Lu3 +) and the tetrathiafulvalene tetrabenzoate linker, which present a new topology and electrical conductivity attributed to S···S interactions observed on ytterbium and lutetium compounds.

The covalent organic frameworks (COFs) arena, reviewed by Shilun Qiu and co-workers, especially focuses on the postsynthetic modifications that increase the complexity by introducing new functionalization and giving rise to modified robust functional COFs for varied functions.

Osamu Terasaki and co-workers show us how the new advancements of electron microscopy can help reveal the crystal structure of less ordered materials like COFs and others thereby minimizing aberrations and sample damage. The authors show how electron microscopy, in combination with powder X-ray diffraction (PXRD), allow the determination of several pristine examples of interwoven nets (COF-505 and COF-112), the electron distributions corresponding to Ar atoms adsorbed in IRMOF-74-V-hex, as well as other examples (MIL-101 and NbO).

Finally, Joseph Hupp and co-workers report less conventional zirconium MOF using tri-phosphonates linkers instead of the well-known tri-carboxylate ones, which shows promising selectivity for separation of CO_2 from N_2.

We are very grateful to Prof. Keinan for the invitation to participate as guest editors of this special issue of the Israel Journal of Chemistry. We also thank Dr. Brian Johnson of Wiley-VCH for his help and counsel. We deeply appreciate the authors' enthusiastic willingness to participate by submitting excellent contributions, to the reviewers for their essential and anonymous labor, and finally to Omar Yaghi for his contributions and enthusiasm to widen this field of chemistry in order to make a better world.


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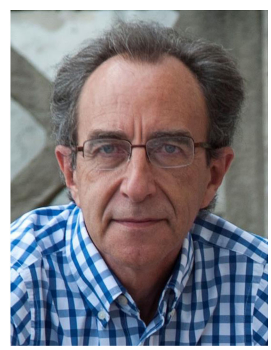
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