

Nanoscience by the Weinstock Group at BGU

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Overview. Numerous important topics in nanoscience can be understood or addressed using 1 to 3 nm sized metal-oxygen cluster anions (polyoxometalates, or POMs), and much of our work involves their use as well defined components for the self-assembly of functional nanostructures.

POMs are prepared from early-transition metals (e.g., V, Mo, and W) in their highest oxidation states (d^0 , and sometimes d^1). Many POMs possess extensive and reversible redox chemistries, and as a class, their compositions and structures, which control the physicochemical properties that impart functionality, can be rationally modified at the atomic level. Functional systems are prepared through incorporation of reactive elements, such as additional transition-metal ions, by control over the nanoscale metal-oxide architectures of larger POM frameworks, and by the use of POM clusters as components of supramolecular and nanoscale assemblies. An overview of new programs in these areas, all initiated at Ben Gurion University, and uniquely associated with the Weinstock laboratory, are summarized below.

Metal-oxide frameworks. In this topic area, a larger (3 nm diameter) oxomolybdate coordination polymer was used to address a fundamental issue in host/guest chemistry: the size-restricted passage of molecules through subnanometer-scale apertures of open-framework structures. In zeolites and rigid functional materials, substrates whose sizes exceed those of the pore dimensions are rigorously excluded. Using a “capsule”-like molybdenum-oxide framework as a soluble analog of porous solid-state (rigid) oxides—e.g., as a soluble analog of 3 Å molecular sieves—we found that branched-alkane carboxylate “guests” (RCO_2^- , $\text{R} = \textit{iso}\text{-Pr}$ and $\textit{tert}\text{-Bu}$) negotiate passage through flexible sub-nanometer Mo_9O_9 apertures whose dimensions (ca. 3 Å) are *smaller* than the entering species (see Cover graphic at right, and Bibliography section, below). More recent work concerns hydrophobic self-assembly and reversible catalysis within metal-oxide framework “nano-reactors”.

Inorganic-ligand monolayers, shells and hollow vesicles.

Using POM clusters (e.g., Fig. 1), we recently provided the first images on inorganic-ligand monolayers on metal nanoparticles (Fig. 2). These findings led to a structural model that includes an important role for counter cations in the molecular-anion ligand shell. Cations play a similar role in organized arrays of molecular anions on planar surface and within the single-molecule walls of macro-anion vesicles.

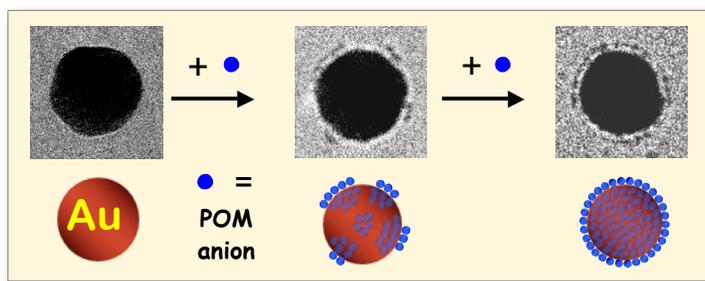
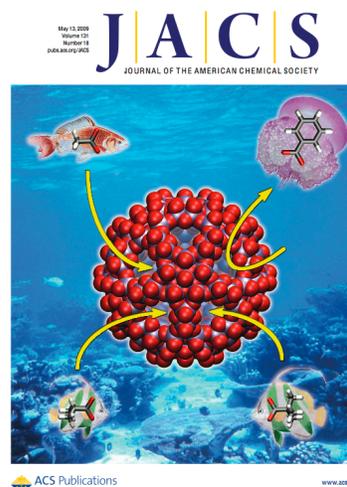


Fig. 2. Evolution (by cryo-TEM) of an inorganic ligand shell on a gold nanoparticle. monolayer (right).



Cover of the *J. Am. Chem. Soc.* issue that features this article.

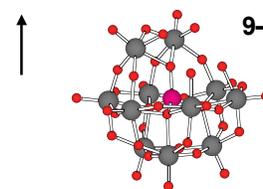


Fig. 1. Structure of $\alpha\text{-AlW}_{11}\text{O}_{39}^{9-}$ (1).

Hence, *our recent findings establish a unifying principle—applicable to organizations on planar surfaces, around metal cores, and within vesicle walls—for better understanding the self-assembly of supramolecular*

structures from charged molecular-inorganic building blocks. (This new principle was recently highlighted on the cover of *Dalton Transactions* (lower right), and led to more recent discoveries of inorganic-shell encapsulated Au-thiol nanoparticles and hollow inorganic vesicles (Fig. 3).

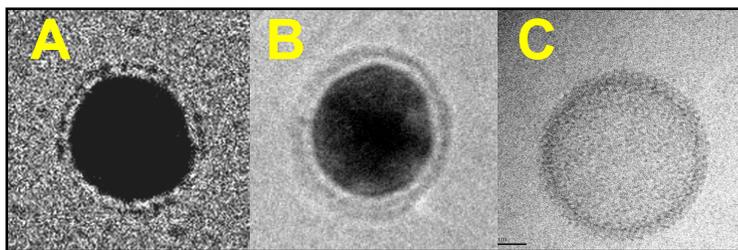


Fig. 3. Cryo-TEM images of spherical arrangements of **1** in water, **A:** on a 14-nm diameter gold NP, **B:** associated with organic cations at the distal ends of mercaptoundecylammonium ligands bound through sulfur to a 14-nm gold particle, and **C:** self-organized into a hollow 180-nm diameter vesicle.

The above work is funded by a grant from the **Israel Science Foundation (ISF)**, entitled, “*Soft inorganic materials: Solution-state studies of metal-oxide superstructures*”.

In parallel with the above, we are investigating the formation, structure and reactions of metal nanoparticles with ligand shells comprised of both inorganic (POM) anions and organic (alkanethiol) ligands. This is in collaboration with Prof. Francesco Stellacci (MIT, Dept. of Materials Engineering), who previously discovered that structurally dissimilar organic ligands gave rise to sub-nanoscale organization on the surfaces of Au NPs, and is funded by a grant from the **U.S.-Israel Binational Science Foundation (BSF)**, entitled, “*Electro-active cluster-anion domains in the organic ligand shells of monolayer-protected metal nanoparticles*”.

POM-stabilized 15-nm AgCl nanocrystals represent an additional class of recently discovered structures. These were prepared by sequential reactions of POM cluster anions, such as α - $K_7PW_{11}O_{39}$ (**K₇2**), with Cl^- and Ag^+ . The resultant clear solution was characterized by cryo-TEM, combined with electron crystallography and darkfield imaging. These findings (*in press*) served as a basis for a recently funded “**ISF Bikura**” application (in collaboration with Louisa Meshi), entitled, “*The structural evolution of nano-ordered functional materials*”.

Summary of current research contracts for support of nanoscience:

German Research Foundation (with Prof. Achim Müller, University of Bielefeld, Germany)

“Soluble Metal Oxide Frameworks: Transport of large organic guests through smaller subnanoscale pores and effects of nano-confinement on hydrophobic self-assembly and organic reactions”

(2011-2013; **\$102,000**)

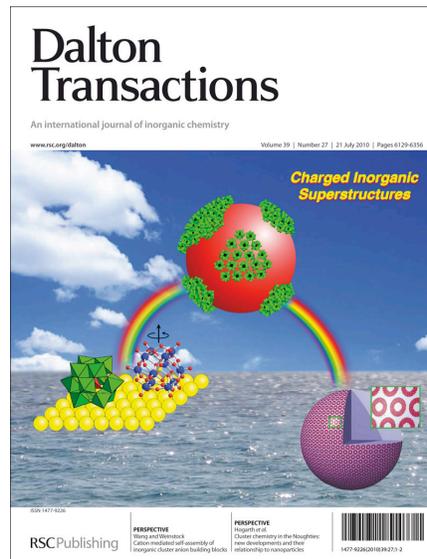
Israel Science Foundation (Focal Initiatives in Research in Science and Technology, FIRST) (With Dr.

Louisa Meshi, BGU Dept. of Materials Engineering): “The structural evolution of nano-ordered functional materials”

(2010-2014; **\$188,000**)

Israel Science Foundation (Individual; 248/09): “Soft inorganic materials: Solution-state studies of metal-oxide superstructures”

(2009-2014; **\$260,000**)



US-Israel Binational Science Foundation; 2008277 (with Prof. Francesco Stellacci, MIT): “Electro-active cluster-anion domains in the organic-ligand shells of monolayer-protected metal nanoparticles” (2009-2014; **\$152,000**)

Editorial activities in nanoscience: Member of the Editorial Board of the Israel Journal of Chemistry, and recently organized a special issue entitled, “Frontiers in Metal-Oxide Cluster Science”. This special issue, whose title is the same as that of an international workshop I hosted earlier this month at the Institute of Advanced Studies in Jerusalem, includes many articles on topics in nanoscience.

Bibliography

Select nanoscience-related publications from the past 36 months

Neyman, A.; Wang, Y.; Sharet, S.; Varsano, N.; Botar, B.; Kögerler, P.; Meshi, L.; Weinstock, I. A. “Polyoxometalate-Directed Assembly of Water-Soluble AgCl Nanocubes” *Chem. Comm. in press*.

Schäffer, C.; Todea, A. M.; Bögge, H.; Cadot, E.; Gouzerh, P.; Kopilevich, S.; Weinstock, I. A.; Müller, A. “Pore and Interior Properties of a Metal-Oxide-Based Capsule Softened: Substituting 60 Oxide by 60 Sulfide Ligands” *Angew. Chem. Int. Ed.* **2011**, *50*, in press.

Müller, A.; Weinstock, I. A. “Frontiers in Metal-Oxide Cluster Science”, Introduction to a special issue of the Israel J. Chem. (Guest Editor, I. A. Weinstock), **2011**, *51*, 176-178.

Snir, O., D.; Wang, Y.; Weinstock, I. A. “The Reduction of Dioxygen by Keggin Heteropolytungstates” *Israel J. Chem.* (special issue—“Frontiers in Metal Oxide Cluster Science”, Weinstock, I. A. Ed.) **2011**, *51*, 247-258.

Petina, O.; Rehder, D.; Haupt, E. T. K. Grego, A.; Weinstock, I. A. Merca, A.; Bögge, H.; Szakacs, J.; Müller, A. “Guests on Different Internal Capsule Sites Exchange with Each Other and with the Outside” *Angew. Chem. Int. Ed.* **2011**, *50*, 410-414.

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Snir, O.; Wang, Y.; Tuckerman, M. E.; Geletii, Y.V.; Weinstock, I. A. “Concerted Proton-Electron Transfer (CPET) to Dioxygen in Water” *J. Am. Chem. Soc.* **2010**, *132*, 11678-11691.

Wang, Y.; Zeiri, Y.; Gitis, V.; Neyman, A.; Weinstock, I. A. “Reversible binding of an inorganic cluster-anion to the surface of a gold nanoparticle” *Inorg. Chim. Acta (Invited article for a special issue in honor of Achim Müller)*, **2010**, *363*, 4416-4420.

Wang, Y.; Weinstock, I. A. “Cation mediated self-assembly of inorganic cluster-anion building blocks” *Dalton Trans. (Invited Perspectives Article)*, **2010**, *39*, 6143-6152.

Highlights: Highlighted on the front cover of the journal.

Wang, Y.; Neyman, A.; Arkhangelsky, E.; Gitis, V.; Meshi, L.; Weinstock, I. A. “Self-assembly and structure of directly imaged inorganic-anion monolayers on a gold nanoparticle” *J. Am. Chem. Soc.*, **2009**, *131*, 17412-17422.

Schäffer, C.; Bögge, H.; Merca, A.; Weinstock, I. A.; Dieter Rehder, D.; Haupt, E. T. K.; Müller, A. “A Spherical 24 Butyrate Aggregate with a Hydrophobic Cavity in a Capsule with Flexible Pores: Confinement Effects and Uptake-Release Equilibria at Elevated Temperatures ” *Angew. Chem. Int. Ed.* **2009**, *48*, 8051-8046.

Ziv, A.; Grego, A.; Kopilevich, S.; Zeiri, L.; Miro, P.; Bo, C.; Müller, A.; Weinstock, I. A. “Flexible Pores of a Metal-Oxide-Based Capsule Permit Entry of Comparatively Larger Organic Guests” *J. Am. Chem. Soc.* **2009**, *131*, 6380-6382.

Highlights: First article from Israel highlighted on the cover of the *Journal* (cover art). See also: *Chemical & Engineering News*, *Chemistry World*, and *SpectroscopyNow.com*, JACS Image Challenge and the first “enhanced” Cover-Art Podcast on JACS Beta.

Neyman, A.; Meshi, L.; Zeiri, L.; Weinstock, I. A. “Direct imaging of the ligand monolayer on an anion-protected metal nanoparticle through cryogenic trapping of its solution-state structure” *J. Am. Chem. Soc.* **2008**, *130*, 16480-16481.

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