The CATALYSIS SOCIETY of Metropolitan New York
www.nycsweb.org

Chairman
Wolfgang Ruettinger
(732) 205-5600
(732) 205-5300 (fax)
Wolfgang.Ruettinger@BASF.com

Secretary
JEFF YANG
732-205-6080
732-635-9478 (fax)
Jeff.Yang@BASF.com

Treasurer
JOHN BRODY
(908) 730-2932
(262) 313-4051 (FAX)
John.f.brody@exxonmobil.com

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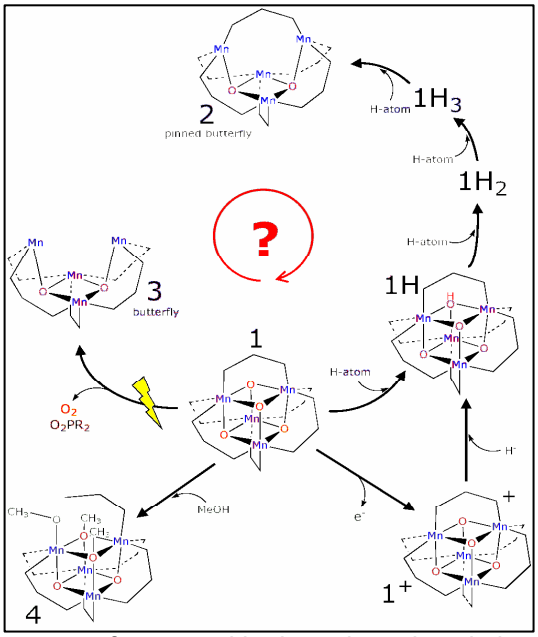
(Formerly Somerset Marriott)

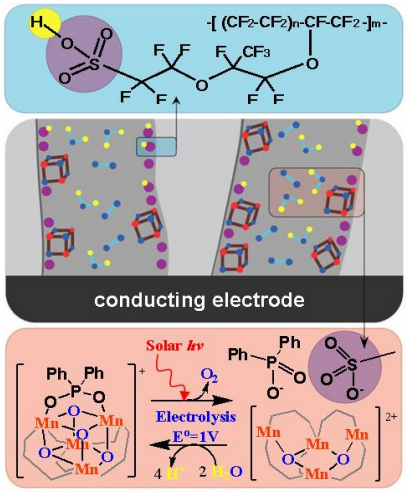
Catalytic Science for Renewable Energy: Bioinspired Catalysts for Solar-Driven Water Splitting

Charles Dismukes
Department of Chemistry & Chemical Biology, and Waksman Institute, Rutgers University

My lecture will cover the current status of research on development of catalysts for electro- and photo-driven water oxidation using base metal catalysts for applications in H_2 production and CO_2 reduction. I will then highlight progress in development of water oxidation catalysts that mimic nature's efficient photosynthetic water-oxidizing enzyme.

Bioinspired Catalysts as Tests of the Chemical Principles of Nature's Photosystem II. The development of sustainable catalysts for production of H_2 or its precursors from renewable sources (water) has been described as the "holy grail" of catalysis. To do so using abundant non-toxic materials possessing long-term stability has been achieved already for 2+ billion years in nature's photosynthetic enzyme. My laboratory is closely linked with the discovery of the Mn_4CaO_x active site used to catalyze photosynthetic water oxidation. Armed with nature's emerging blueprint we have synthesized a family of bioinspired molecular complexes that attempt to capture the essential catalytic features of this enzyme. As primary example, we have synthesized a family of manganese-oxo molecular complexes containing the "cubane" core ($[M_4O_4]^{5+/6+/7+}$). These complexes exhibit extraordinary reactivity as oxidation catalysts, being capable of C-H bond cleavage of saturated hydrocarbons in solution and oxo transfer to various substrates. Cubiums (7+ core) perform heterolytic cleavage of N-H bonds greater than 127 kcal/mol. Most relevant is their reactivity in O_2 evolution in the gas phase, and their reductive elimination of water upon reduction in solution (Figure). Their metrical and electronic structures have been characterized by a range of physico-chemical methods leading to a clear picture of how these reactions occur. However, catalytic O_2 evolution had evaded us until we learned how to deal with protons and the barrier to O-O bond formation.





Solar Cell for Water Splitting. **C**atalytic water oxidation for thousands of turnovers was achieved by placing the cubium cluster into the aqueous channels of proton-conducting membranes (Nafion) which contain ionizable sulfonic acid groups. Our first incarnation of these cells used an applied electrical potential to oxidize water bound to the catalyst/Nafion/electrode assembly, plus light to release the O_2 from the cubium core. Our recently published work has demonstrated the functioning of these molecules upon integration into photovoltaic cells (dye-sensitized TiO_2 cells) that use only solar radiation as the energy source.

Catalysts in Development: Definitive testing of the bioinspired concept has led us to examine inorganic solids possessing the cubical M_4O_4 topology, but otherwise lacking an organic ligand framework. The discovery of conditions that activate a well known class of inert inorganic solids to become catalysts for water oxidation will be presented.