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Swiss Science Concentrates

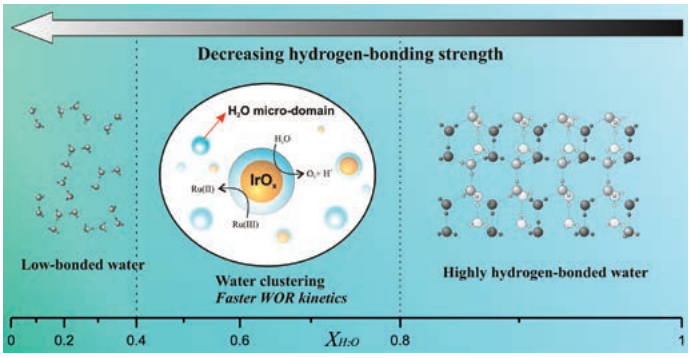
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Catalysis of Water Oxidation in Acetonitrile by Iridium Oxide Nanoparticles

J.C. Hidalgo-Acosta, M.A. Méndez, M.D. Scanlon, H. Vrubel, V. Amstutz, W. Adamiak, M. Opallo, and H.H. Girault*, *Chem. Sci.* **2015**, *6*, 1761. EPF Lausanne

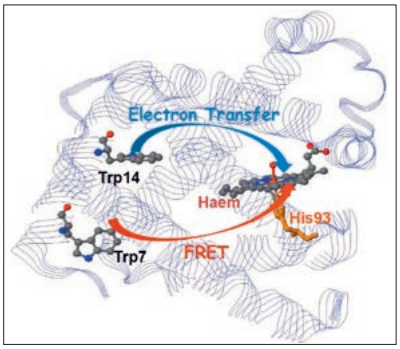
Much effort is currently being devoted to the production of environmentally friendly solar fuels *via* water splitting. Of the two half-reactions – the hydrogen evolution reaction and the water oxidation reaction – the latter is considered the bottleneck of water splitting. Girault and coworkers studied H_2O oxidation catalysed by iridium oxide nanoparticles (IrO_2 NPs) in different water–acetonitrile mixtures using $[Ru^{III}(bpy)_3]^{3+}$ as oxidant. The results clearly demonstrate that IrO_2-catalyzed water oxidation is dependent on the water content for water–acetonitrile mixtures, equimolar proportions of water and acetonitrile being optimal. Additionally, the use of water–acetonitrile mixtures appears a viable alternative to enhance the stability of redox shuttles, a fundamental problem in photocatalytic water oxidation systems.



Tryptophan-to-Heme Electron Transfer in Ferrous Myoglobins

R. Monni, A. Al Haddad, F. van Mourik, G. Auböck, and M. Chergui*, *PNAS* **2015**, *112*, 5602. EPF Lausanne

Many biochemists and biologists use the amino-acid residue tryptophan (Trp) as donor in Fluorescence Resonant Energy Transfer (FRET) studies of protein dynamics, assuming that its fluorescence decay is entirely due to FRET. The decay is then used as a measure of the distance to an acceptor chromophore.

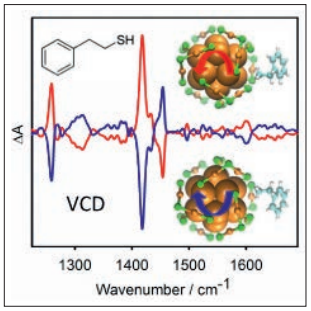


However, the assumption of FRET is not always valid and in this contribution, the group of Prof. M. Chergui shows that in some cases, Trp fluorescence quenching is due to electron transfer rather than FRET. This behaviour is confirmed for Trp14 in all myoglobins, and is a warning to biologists, as if this situation occurs in other proteins, it would give out false readings that can be mistaken for conformational changes of proteins.

Chirality Transfer from Gold Nanocluster to Adsorbate Evidenced by Vibrational Circular Dichroism

I. Dolamic, B. Varnholt, and T. Bürgi*, *Nat. Commun.* **2015**, *6*, 7117. University of Geneva

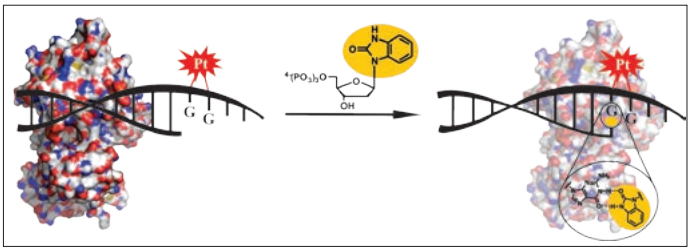
The chirality of extended metal surfaces and of their nanometer size analogous, metallic nanoparticles and clusters, has become an emerging field of research. Bürgi and coworkers separated the enantiomers of an intrinsically chiral thiolate-protected gold cluster, $Au_{38}(2\text{-PET})_{24}$ (2-PET=2-phenylethylthiolate) using chiral HPLC. The chirality of the cluster arises from the arrangement of the thiolates on the cluster surface. The thiolates themselves however, are achiral. Using vibrational circular dichroism (VCD) it is then shown that the cluster can transfer its chirality to the adsorbed achiral molecules. When adsorbed on the cluster the latter adopt preferentially a chiral conformation. Such chirality transfer from metals to adsorbates likely plays an important role in heterogeneous enantioselective catalysis.



Nucleotides with Altered Hydrogen Bonding Capacities Impede Human DNA Polymerase η by Reducing Synthesis in the Presence of the Major Cisplatin DNA Adduct

A. Nilforoushan, A. Furrer, L.A. Wyss, B. van Loon and S. J. Sturla*, *J. Am. Chem. Soc.* 2015, *137*, 4728. ETH Zürich

Human DNA polymerase η (hPol η) contributes to anticancer drug resistance by catalyzing the replicative bypass of cisplatin DNA adducts. In this study, Sturla and coauthors demonstrated how synthetic nucleoside triphosphates act as hPol η substrates. This is the first example of hPol η inhibition in the presence of a platinated DNA template. The single nucleotide incorporation efficiency of the altered nucleotides varied by more than 10-fold and the higher incorporation rates appeared to be attributable to the presence of an additional hydrogen bond between incoming dNTP and templating base. The findings may lead to novel therapeutics developed to overcome platinum drug resistance in cancer therapy.



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