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Swiss Science Concentrates

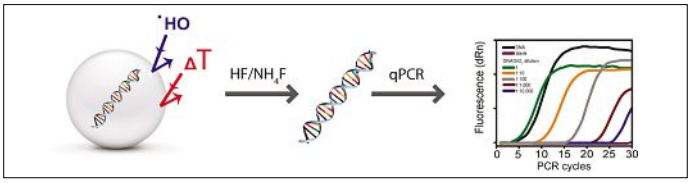
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Protection and Deprotection of DNA — High-Temperature Stability of Nucleic Acid Barcodes for Polymer Labeling

D. Paunescu, R. Fuhrer, and R. N. Grass*, *Angew. Chem. Int. Ed.* **2013**, *52*, 4269. ETHZ

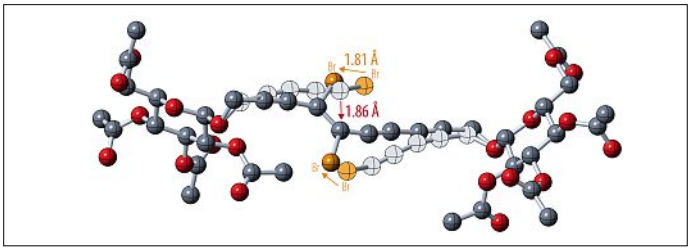
DNA not only encodes the information of life, but can also be used as a data storage device for nanotechnical applications. However, DNA is prone to degradation *e.g.* by elevated temperatures and exposure to sunlight *etc.* The authors present an elegant method to stabilize DNA: DNA is adsorbed to silica nanoparticles. These are subsequently treated to add a thin silicate layer around the particles. The resulting DNA-loaded nanoparticles are extremely resistant: they can be added to melt-processed polymers at 200 °C and the encapsulated DNA is protected against i) reactive oxygen species, ii) degradation at elevated temperatures and iii) UV degradation. Downstream recovery of DNA is achieved by treatment with hydrofluoric acid which dissolves the silica, leaving the DNA intact. Analysis can be achieved thanks to polymerase chain reaction amplification. The silica-encapsulated DNA is therefore ideally suited as security tag of consumer products against counterfeits.



A Multistep Single-Crystal-to-Single-Crystal Bromodiacetylene Dimerization

T. N. Hoheisel, S. Schrettl, R. Marty, T. K. Todorova, C. Corminboeuf, A. Sienkiewicz, R. Scopelliti, W. B. Schweizer, and H. Frauenrath*, *Nature Chemistry* **2013**, *5*, 327. EPFL

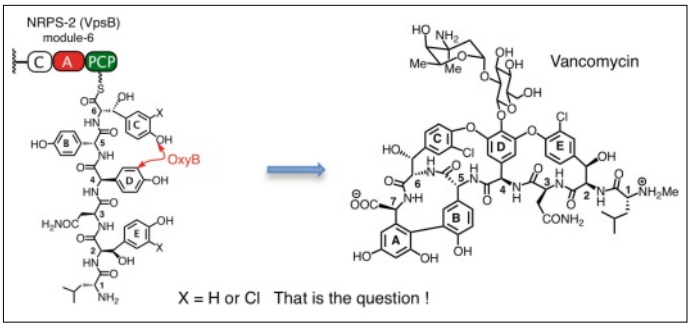
When organic molecules are confined in the environment of a crystalline structure, they often display unusual properties and reactivity. Frauenrath and co-workers describe a novel topochemical dimerization of bromoacetylenes that occurs in the solid state upon irradiation with UV light as a single-crystal-to-single-crystal transformation. This reaction takes place with no need for reagents or solvent and with minimal changes of the lattice parameters, yielding the novel carbon-rich (*E*)-1,2-dibromoeneynes. Investigations by means of UV-Vis, NMR and ESR spectroscopic methods coupled with DFT calculations led to the proposal of a reaction mechanism involving four steps after excitation, including a [2+1] photocycloaddition and a 1,2-bromine shift. Reactions on a preparative scale could also be accomplished in good yield.



Substituent Effects on the Phenol Coupling Reaction Catalyzed by the Vancomycin Biosynthetic P450 Enzyme OxyB

P. C. Schmartz, K. Wölfel, K. Zerbe, E. Gad, E. S. E. Tamany, H. K. Ibrahim, K. Abou-Hadeed, and J. A. Robinson*, *Angew. Chem. Int. Ed.* **2012**, *51*, 11468. University of Zürich and University of Suez-Canal (EG)

Vancomycin has captivated chemists for over half a century. Besides its remarkable antibiotic activity and complex chemical architecture, its biosynthesis is of particular interest. In this context, Robinson and co-workers report on the oxidative phenol coupling reactions, which are required to generate the cross-linked heptapeptide backbone of vancomycin. Their study demonstrates that the reaction rate of the first cross-linking reaction, catalyzed by the cytochrome P450 enzyme OxyB, is much slower when a chloride substituent is present. This suggests that vancomycin is biosynthetically chlorinated after the oxidative coupling has taken place.



Ultrafast Tryptophan-to-Heme Electron Transfer in Myoglobins Revealed by UV 2D Spectroscopy

C. Consani, G. Auböck, F. van Mourik, and M. Chergui*, *Science* **2013**, *339*, 1586. EPFL

Deciphering electron transfer (eT) mechanisms within metalloproteins is critical towards the understanding of key biological redox processes whereby eT must be exquisitely orchestrated. Chergui and coworkers report a time-resolved spectroscopic investigation of the decay pathways of two critical tryptophan residues (Trp) in ferric myoglobins: MbCN and metMb. While the fluorescence decay of Trp7 and Trp14 was previously attributed to an energy transfer (FRET) to the heme, the authors identify that Trp14 decays by eT to the heme. In this case, the distance between the tryptophan donor and the heme acceptor is <10 Å and the transfer must thus occur either by a tunneling- or a hopping process. Their findings raise the question as to whether such electron transfers may be a frequent phenomenon in other protein classes.

Prepared by Nico Bruns, Patrick Burch, Valentin Köhler, Raphael Reuter, Paolo Tosatti and Thomas R. Ward
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