



Swiss Science Concentrates

A CHIMA Column

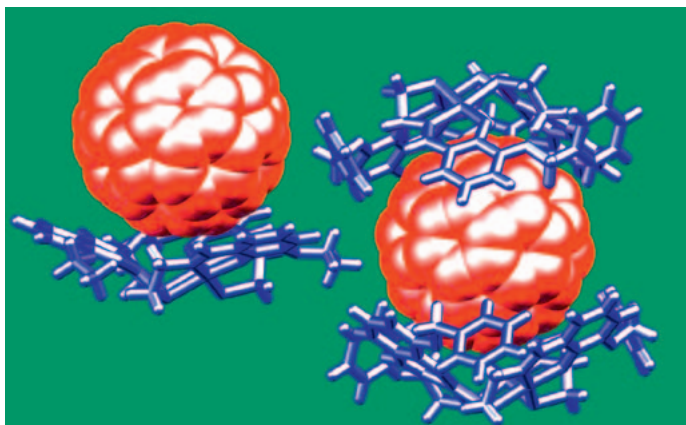
Short Abstracts of Interesting Recent Publications of Swiss Origin

Metallohosts with a Heart of Carbon

E. C. Constable*, G. Zhang, D. Häussinger, C. E. Housecroft*, J. A. Zampese, *J. Am. Chem. Soc.* **2011**, *133*, 10776.

University of Basel

Metal-templated Schiff-base condensation is an ideal playground to generate supramolecular architectures. The authors report on a one-pot assembly of a trinuclear Ni₃S₃-concave complex able to fix host molecules such as CH₂Cl₂ or C₆₀. Depending on the nature of the substituents on a pending arm of the tridentate ligand, the size and the shape of the supramolecular guest can be varied to yield either a bowl (1:1) or a capsule (2:1 stoichiometry) around C₆₀, as evidenced by NMR titration.

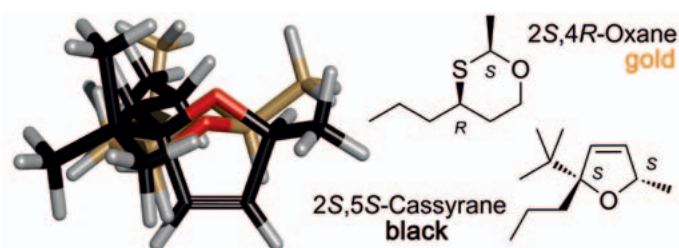


Cassis Odor through Microwave Eyes: Olfactory Properties and Gas-Phase Structures of all the Cassyrane Stereoisomers and its Dihydro Derivatives

H. Mouhib, W. Stahl*, M. Lüthy, M. Büchel, P. Kraft*, *Angew. Chem. Int. Ed.* **2011**, *50*, 5576.

RWTH Aachen and Givaudan Schweiz

This article demonstrates the usefulness of gas-phase structures for structure–odor correlations. Since the odor critically depends on the stereochemistry of a molecule, the authors determined the gas phase structures of all four stereoisomers of Cassyrane and its dihydro derivatives by a combination of microwave spectroscopy and quantum-chemical calculations. Superposition analyses (see below) revealed the importance of the 5*S*-configuration for a cassis odor, while the 2*S*,5*R*-isomer was found the most intense.

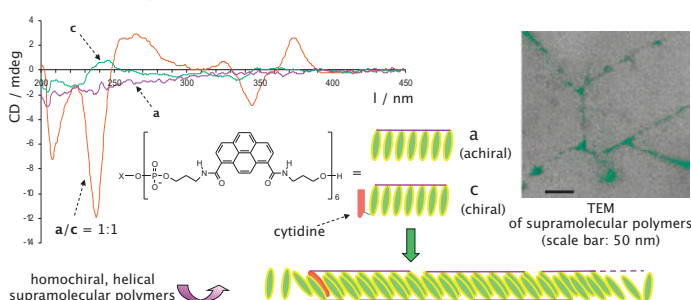


Amplification of Chirality by Supramolecular Polymerization of Pyrene Oligomers

A. L. Nussbaum, D. Studer, V. L. Malinovskii, R. Häner*, *Angew. Chem. Int. Ed.* **2011**, *50*, 5490.

University of Bern

Chiral amplification is a key requirement for the emergence of life. Supramolecular polymerization of achiral heptamers (α) consisting of phosphodiester-linked pyrene units, in the presence of sub-stoichiometric amounts of chiral inductor heptamers (χ) bearing a single terminal 2'-deoxycytidine led to the slow development of anisotropy as evidenced by CD spectroscopy. The supramolecular helical structures result from interstrand π -stacking interactions. Highest anisotropy factors were found in the presence of smaller quantities of the chiral inductor, namely at a ratio of 80:20 (α : χ).



Organocatalyzed Michael Addition of Aldehydes to Nitro Alkenes – Generally Accepted Mechanism Revisited and Revised

K. Patora-Komisarska, M. Benohoud, H. Ishikawa, D. Seebach*, Y. Hayashi*, *Helv. Chim. Acta* **2011**, *94*, 719.

Tokyo University of Science, Japan and ETH-Zürich

Organocatalysis often requires high catalyst loadings. In a thorough mechanistic study of the above *Michael* addition reaction, Seebach, Hayashi and coworkers have identified amino-nitrocyclobutane intermediates. These off-cycle ‘resting states’ of the catalyst are in equilibrium with iminium-nitronate zwitterions **5**, protonation of which was identified as the rate-determining step of the catalytic cycle. A judiciously selected acid drives the catalyst out of the unproductive cyclobutane intermediate, thus allowing for decrease of the catalyst loading to 1%.

