



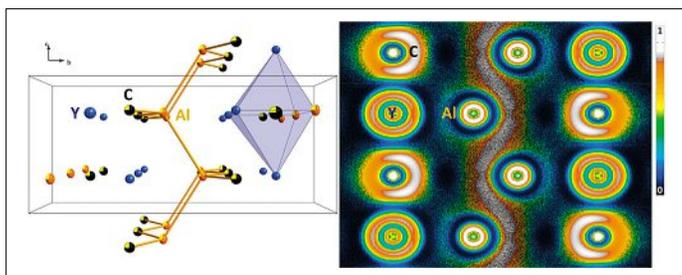
Swiss Science Concentrates

A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

YAIC: A Bonding Chameleon with Heteropolyacetylene Features

M. R. Kotyrba*, E. Cuervo-Reyes*, and R. Nesper*, *Angew. Chem. Int. Ed.* **2015**, *54*, 9606. ETH Zürich and EMPA Dübendorf Silicon carbide and aluminium carbide are extremely stable refractory compounds demonstrating the strength of the Si–C and the Al–C bonds, respectively. Kotyrba, Cuervo-Reyes and Nesper describe a novel ternary aluminide–carbide, YAIC, which was prepared by a flux method. It crystallizes as a partially filled-up TII structure, showing remarkable structural aspects at the border between Zintl phases and intermetallics. The compound represents a fascinating compromise between the polarized metal (stuffed intermetallic) and the semicovalent $Y^{3+}[AlC]^{3-}$ model. A key feature is the coexistence of two-centre and multi-centre bonds. The latter appear as tapes meandering wherever there would be a direct Al–Al or Y–Al contact, and contain the residual electron density after the formation of the Al–C semi-covalent chains.

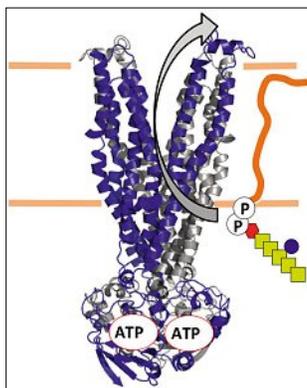


Structure and Mechanism of an Active Lipid-linked Oligosaccharide Flippase

C. Perez, S. Gerber, J. Boilevin, M. Bucher, T. Darbre, M. Aebi, J.-L. Reymond, and K. P. Locher*, *Nature*, **2015**, *524*, 433. ETH Zürich

The flipping of membrane-embedded lipids containing large, polar head groups is slow and energetically unfavourable, and is therefore catalysed by flippases, the mechanisms of which are unknown. A prominent example of a flipping reaction is the translocation of lipid-linked oligosaccharides that serve as donors in *N*-linked protein glycosylation.

In *Campylobacter jejuni*, this process is catalysed by the ABC transporter PglK. Locher and coauthors present a mechanism of PglK-catalysed, lipid-linked oligosaccharide flipping based on crystal structures in distinct states, a newly devised *in vitro* flipping assay, and *in vivo* studies. The proposed mechanism is distinct from the classical alternating-access model observed in other transporters.

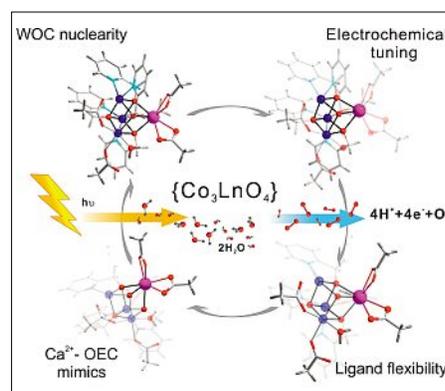


3d–4f $\{Co^{II}_3Ln(OR)_4\}$ Cubanes as Bio-Inspired Water Oxidation Catalysts

F. Evangelisti, R. Moré, F. Hodel, S. Luber*, and G. R. Patzke*, *J. Am. Chem. Soc.* **2015**, *137*, 11076. University of Zürich

The $\{CaMn_4O_5\}$ oxygen evolving complex of photosystem II represents a major paradigm for the development of water oxidation catalysts (WOCs). However, translating its key features into active molecular WOCs remains a major challenge.

Patzke, Luber and co-workers now introduce $[Co^{II}_3Ln(hmp)_4(OAc)_5H_2O](\{Co^{II}_3Ln(OR)_4\}; Ln=Ho–Yb, hmp=2-(hydroxymethyl)pyridine)$ cubanes as new functional and stable model systems to explore a range of crucial design parameters, including core nuclearity, redox-inactive promoters, and ligand exchange properties. The highly active $\{Co^{II}_3Ln(OR)_4\}$ cubanes advance promote bio-inspired design through the combination of Ln^{3+} core cations as redox-inactive Ca^{2+} analogues of nature's oxygen evolving complex with flexible aqua-/acetate ligands. The Ln^{3+} -enhanced ligand exchange of the $\{Co^{II}_3Ln(OR)_4\}$ WOCs is substantiated with molecular dynamics studies.



Synthesis of Fijiolide A via an Atropselective Paracyclophane Formation

C. Heinz and N. Cramer*, *J. Am. Chem. Soc.* **2015**, *137*, 11278. EPF Lausanne

Fijiolide A is a secondary metabolite isolated from a marine-derived actinomycete displaying inhibitory activity against TNF- α -induced activation of NF κ B, an important transcription factor and a potential target for the treatment of different cancers and inflammation related diseases. Fijiolide A is a glycosylated complex paracyclophane, which is structurally closely related to the Bergman-aromatization product of enediyne C-1027. Cramer and Heinz report an enantioselective synthesis of fijiolide A demonstrating the power of fully intermolecular ruthenium-catalysed [2+2+2]-cyclotrimerizations with three different alkynes to assemble the heavily substituted central arene core. The characteristic strained [2.6]-paracyclophane structure is accessed by a templated atropselective macroetherification reaction.

