



Swiss Science Concentrates

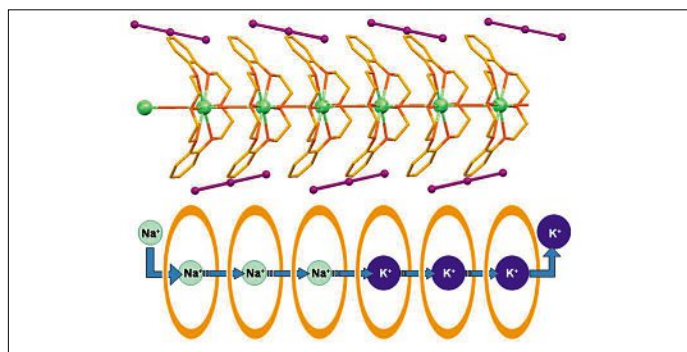
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Kinetics of Ion Transport through Supramolecular Channels in Single Crystals

C. D. Assouma, A. Crochet, Y. Ch ermond, B. Giese, and K. M. Fromm*, *Angew. Chem. Int. Ed.* **2013**, *52*, 4682. University of Fribourg

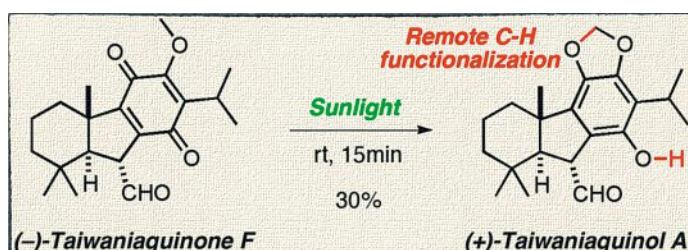
Crown ethers form 1D stacks in single crystals and therefore provide potential channels for ion transport. However, reactions and ion exchanges processes in single crystals most often result in their disassembly. Now, the authors report crystalline supramolecular channels in which trihalide ions act as scaffold. Importantly, in the absence of these trihalide ions, no stacking is observed. These single crystals allow ion exchange of K^+ with Na^+ in their channels, without disturbing the structural integrity of the single crystal. The process is very fast, with an activation energy of only $27 \text{ kJ}\cdot\text{mol}^{-1}$. This is comparable to the energy barriers encountered in superionic conductor materials.



Syntheses of Taiwaniaquinone F and Taiwaniaquinol A via an Unusual Remote C–H Functionalization

C. Thommen, C. K. Jana, M. Neuburger, and K. Gademann*, *Org. Lett.* **2013**, *15*, 1390. University of Basel

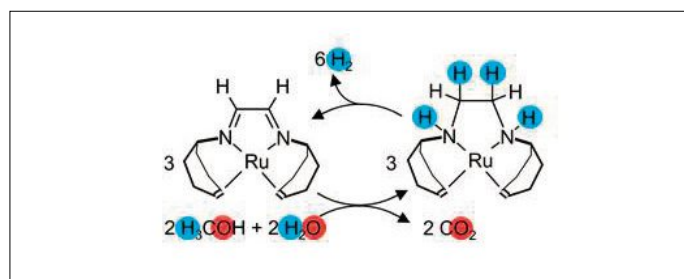
Thommen *et al.* report a protecting-group-free total synthesis of (–)-taiwaniaquinone F from abietic acid in 17 steps. Most interestingly, they demonstrate that the quinone is transformed *via* a redox neutral rearrangement into the methylenedioxy bridged (+)-taiwaniaquinol A by exposure to sunlight. The fact that the quinone is found in the bark and its natural congener, the quinol in the leaves of *Taiwania cryptomoides* where sunlight exposure is ensured, suggests that this remote C–H functionalization is part of the biogenesis of this natural product.



A Homogeneous Transition Metal Complex for Clean Hydrogen Production from Methanol–Water Mixtures

R. E. Rodriguez-Lugo, M. Trincado, M. Vogt, F. Tewes, G. Santiso-Quinones, and H. Gr utzmacher*, *Nature Chem.* **2013**, *5*, 342. ETHZ

Gr utzmacher and coworkers present an homogenous Ru-based catalyst for the clean conversion of methanol and water to carbon dioxide and hydrogen gas. The reaction does not produce unwanted carbon monoxide, which usually poisons the catalyst. The catalyst incorporates a chemically non-innocent azadiene ligand, which acts as a hydrogen acceptor during the catalytic cycle. This versatile catalyst allows to extract the entire hydrogen content of both substrates (*i.e.* 12% by weight) and thus may be attractive for the development of electrodes for methanol-based fuel cells.



Bicyclic Peptide Ligands Pulled out of Cysteine-rich Peptide Libraries

S. Chen, J. R. Rebollo, S. A. Buth, J. Morales-Sanfrutos, J. Touati, P. G. Leiman, and C. Heinis*, *J. Am. Chem. Soc.* **2013**, *135*, 6562. EPFL

Bicyclic peptides are attractive, structurally diverse ligands to bind protein targets. Linking their genotype and phenotype can be achieved thanks to phage display, thus allowing to screen large peptide libraries. By randomizing amino acids between three cysteine residues and subsequent oxidative cyclization with a fourth randomized cysteine, libraries of bicyclic peptides with a wide range of topologies were obtained. Affinity screening against human urokinase-type plasminogen activator (uPA) yielded, after only two rounds of panning, an inhibitor that binds with a 7-fold higher affinity than the best monocyclic human uPA inhibitor. This technically simple procedure should find broad applications for the generation of peptide ligands.

