



## Swiss Science Concentrates

A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

### Assembling Multiporphyrin Stacks Inside the DNA Double Helix

M. Vybornyi, A. L. Nussbaumer, S. M. Langenegger, and R. Häner\*, *Bioconjugate Chem.* **2014**, *25*, 1785. University of Bern

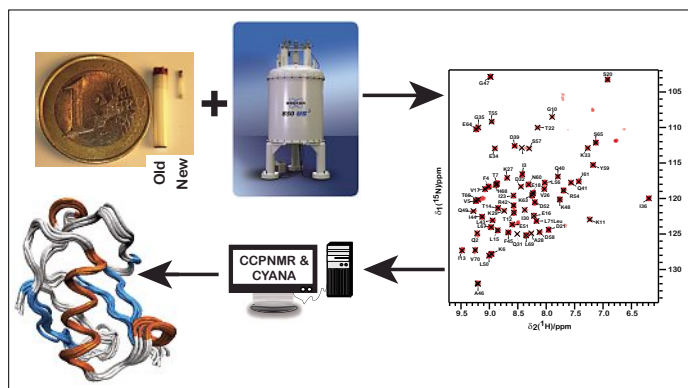
Light-harvesting complexes consist of an exquisite supramolecular assembly of porphyrins embedded within macromolecules. In a biomimetic spirit, Häner and co-workers describe an incorporation strategy of up to four porphyrins into double-stranded DNA-hybrids without disturbing the B-DNA structure. Pairwise placement of porphyrins in opposite positions maintains duplex stability *via*  $\pi$ -stacking interactions. In contrast, a considerable reduction in the  $T_m$  is observed when porphyrins are positioned opposite to natural nucleobases. Optical spectroscopy provides strong support for an H-type interaction. The present findings demonstrate the value of DNA for the controlled formation of molecularly-defined porphyrin assemblies.



### De Novo 3D Structure Determination from Sub-milligram Protein Samples by Solid-State 100 kHz MAS NMR Spectroscopy

V. Agarwal, S. Penzel, K. Szekely, R. Cadalbert, E. Testori, A. Oss, J. Past, A. Samoson, M. Ernst, A. Böckmann, and B. H. Meier\*, *Angew. Chem.* **2014**, *53*, 12253. ETH Zurich

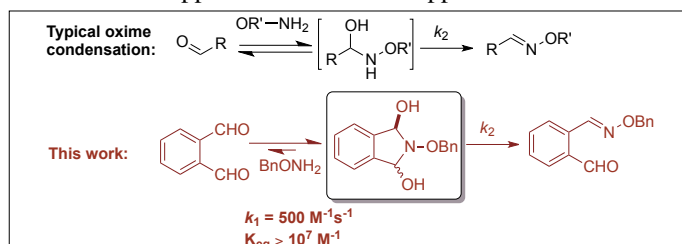
Solid-state NMR spectroscopy is one of the most important characterization tools for structural studies of proteins. Unfortunately, this technique typically requires large amounts of sample (*e.g.* 20 mg). Meier and coworkers outline a strategy that allows to overcome this limitation by relying on a new NMR probe pushing magic angle rotation frequencies to around 100 kHz. This significantly increases the sensitivity and spectral resolution for efficient proton detection. Using the new method, a well-defined structure of ubiquitin as a model protein was obtained using only 500  $\mu\text{g}$ .



### Dialdehydes Lead to Exceptionally Fast Bioconjugations at Neutral pH by Virtue of a Cyclic Intermediate

P. Schmidt, L. Zhou, K. Tishinov, K. Zimmermann, and D. Gillingham\*, *Angew. Chem. Int. Ed.* **2014**, *53*, 10928. University of Basel

Identifying reactions that proceed fast under neutral pH and in highly dilute solution is a standing challenge in chemical biology. Gillingham and coworkers present an exceptionally fast uncatalyzed reaction between dialdehydes and *O*-alkylhydroxylamines. At neutral pH, it proceeds at rates of  $500 \text{ M}^{-1}\text{s}^{-1}$ . A highly stable cyclic intermediate is formed, which ultimately undergoes dehydration to yield an oxime. The initial addition step thereby becomes effectively irreversible, making the timing of the typically slow subsequent dehydration step immaterial. This highly efficient bioconjugation strategy may find numerous application for *in vitro* applications.



### Water Photolysis at 12.3% Efficiency via Perovskite Photovoltaics and Earth-abundant Catalysts

J. Luo, J.-H. Im, M. T. Mayer, M. Schreier, M. K. Nazeeruddin, N.-G. Park, S. D. Tilley, H. J. Fan, and M. Grätzel\*, *Science* **2014**, *345*, 1593. EPFL Lausanne

Perovskite-based solar cells have emerged as a promising alternative to silicon-based solar cells. In their recent publication Grätzel and coworkers combine a state-of-the-art perovskite tandem solar cell with a water splitting device to produce hydrogen gas and oxygen. The catalyst electrodes, based on a NiFe-layered double hydroxide, and thus relying on cheap and abundant materials, possess high activity towards both hydrogen and oxygen evolution. A remarkable total solar-to-hydrogen efficiency of 12.3% is obtained with such low cost devices.

