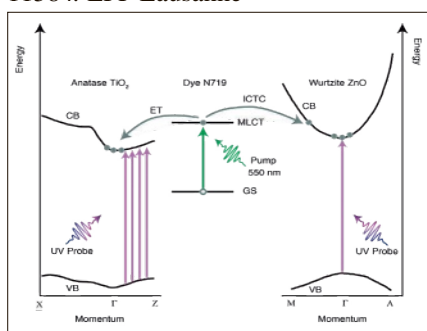


CH Swiss Science Concentrates

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Short Abstracts of Interesting Recent Publications of Swiss Origin

Interfacial Electron Injection Probed by a Substrate-Specific Excitonic Signature

E. Baldini, T. Palmieri, T. Rossi, M. Oppermann, E. Pomarico, G. Auböck, and M. Chergui*, *J. Am. Chem. Soc.* **2017**, *139*, 11584. EPF Lausanne



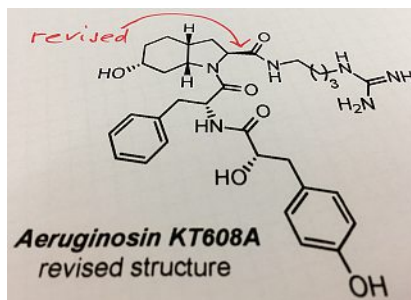
A better understanding of interfacial electron transfer (ET) remains crucial for the creation of advanced materials with potential applications in solar energy conversion and photocatalysis. To address this problem, Chergui and co-workers present a

new approach with femtosecond resolution to probe interfacial ET in sensitized transition metal oxides (TiO₂ and ZnO) by looking at the response of their excitonic transitions. By using broadband deep-UV pulses, they show that upon electron injection into TiO₂, long-range Coulomb screening determines the excitonic transitions, while in ZnO it is phase-space filling. This method offers an elegant route to probe interfacial ET with solid state sensitizers.

Total Synthesis and Structural Revision of Aeruginosin KT608A

M. Scherer and K. Gademann*, *Org. Lett.* **2017**, *19*, 3915. University of Zurich

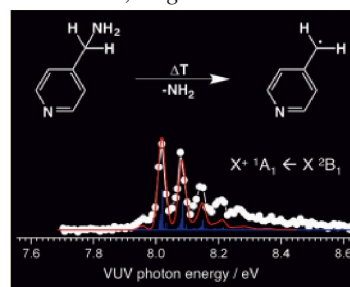
The total synthesis of naturally derived molecules is an invaluable tool in establishing their real structure with a precise assignment of all stereogenic centers. Scherer and Gademann reported on the total synthesis of aeruginosin KT608A, a tetrapeptide isolated from *Microcystis aeruginosa* bloom material. The unusual *D*-diepi-configuration of the 6-hydroxyoctahydroindole-2-carboxylic acid (Choi) core was prepared *via* C–H activation followed by heterogeneous hydrogenation. Careful spectral analysis of the synthesized and isolated molecules unexpectedly led to the revision of the structures of aeruginosin KT608A and six additional aeruginosins.



The revised structure has a different configuration at position 2 of the Choi motif. The paper highlights the value of total synthesis for the unambiguous assignment of correct configurations in complex natural molecules.

Isomer-Selective Generation and Spectroscopic Characterization of Picolyl Radicals

E. Reusch, F. Holzmeier, P. Constantinidis, P. Hemberger*, and I. Fischer*, *Angew. Chem. Int. Ed.* **2017**, *56*, 8000. PSI Villigen



Nitrogen-containing, resonance-stabilized radicals play an important role as reactive intermediates in the combustion of biofuels, as well as in astrochemistry. Spectroscopic data of these compounds are rather scarce because their isomer-selective generation is often

difficult. Hemberger, Fischer and co-workers now present the preparation of the three picolyl radical isomers (C₅H₄N-CH₂*) through deamination by flash pyrolysis from the respective aminomethylpyridine precursors. Threshold photoelectron spectra, obtained at the vacuum ultraviolet (VUV) beamline of the Swiss Light Source, exhibit distinct ionization energies and vibrational fine-structure that can be assigned to a totally symmetric ring deformation mode. The obtained data can be used to distinguish different picolyl isomers in on-line combustion analysis and further, to study the chemistry of picolyl radicals and their kinetics.

Privileged Structures Revisited

P. Schneider and G. Schneider*, *Angew. Chem. Int. Ed.* **2017**, *56*, 7971. ETH Zurich

Privileged structures are described as scaffolds which can be functionalized in many ways, such that the resulting products bind to different receptors. G. Schneider and P. Schneider analyzed a database containing 1.4 million bioactive compounds, with the aim of finding the prevalence of certain molecular frameworks. Quantification of the chemical scaffold diversity was done by using the Shannon entropy formalism. The analysis revealed an apparent inverse relationship between the number of hydrogen-bond acceptors of a scaffold and its potential to bind different targets. Further results suggest that chemically easily accessible scaffolds can serve as templates for the generation of compounds which could bind to almost all target families. The study places the concept of privileged structures into a critical context and is relevant for target-focused library design.

