



Swiss Science Concentrates

A CHIMIA Column

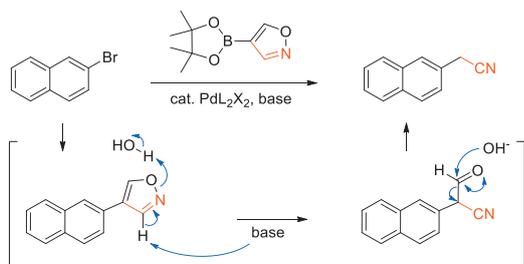
Short Abstracts of Interesting Recent Publications of Swiss Origin

Palladium-Catalyzed Cyanomethylation of Aryl Halides through Domino Suzuki Coupling-Isoxazole Fragmentation

J. Velcicky*, A. Soicke, R. Steiner, H.-G. Schmalz*, *J. Am. Chem. Soc.* **2011**, *133*, 6948

Novartis, Basel and University of Cologne

The authors report a straightforward one-pot protocol for the cyanomethylation of aryl halides. For this purpose they exploit a palladium-catalyzed reaction using commercially available isoxazole-4-boronic acid pinacol ester. The process proceeds *via* Suzuki cross-coupling followed by a base-induced isoxazole fragmentation. This original domino-reaction opens easy access to a broad range of arylacetonitriles based on an operationally simple and reliable route.

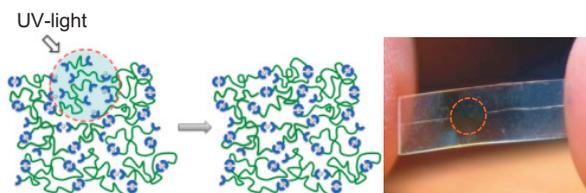


Optically Healable Supramolecular Polymers

M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan, C. Weder*, *Nature* **2011**, *472*, 334

Case Western Reserve University, US Army Research Laboratory, USA, and University of Fribourg

Self-healing polymers that repair themselves when damaged are able to extend the lifetime of materials and can contribute to avoid catastrophic material failure. Most self-healing mechanisms require heating. The authors now developed materials that heal upon illumination with light. These polymers were made by supramolecular polymerization of ligand-terminated monomers with metal complexes. The complexes connect the monomers in a non-covalent manner. They also act as local heat sources, as they absorb light and convert it to heat. This causes dissociation of the metal-ligand complexes and melting of the material. The low molecular weight makes for low viscosity and therefore effective healing. The damaged material regains its full strength and the healing even works under load.



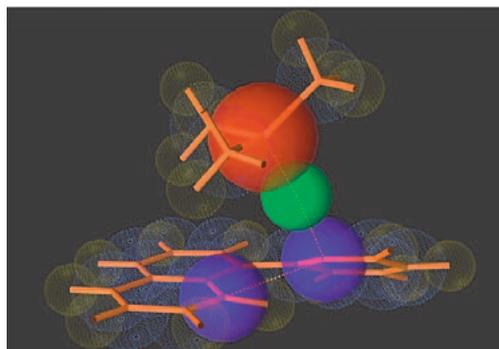
(Figure courtesy of Gina Fiore for Adolphe Merkle Institute, Case Western Reserve University, US Army Research Laboratory)

Proton-Catalyzed, Silane-Fueled Friedel-Crafts Coupling of Fluoroarenes

O. Allemann, S. Duttwyler, P. Romanato, K. K. Baldrige, J. S. Siegel*, *Science* **2011**, *332*, 574

University of Zurich

Traditional Friedel-Crafts reactions append alkyl or acyl groups to aromatic rings, but do not couple arenes due to the inaccessibility of phenyl cations. Now, phenyl-cation equivalents, generated from normally unreactive aryl fluorides by Lewis acidic silyl cations, effect intramolecular arene coupling. The in road to the silyl cation begins with a neutral silane and catalytic super acid; the exchange of C-F for Si-F bond enthalpies provides the driving force. The methodology is applicable to the synthesis of polynuclear aromatic hydrocarbons, such as tailored graphenes, fullerene fragments, and carbon tubes.

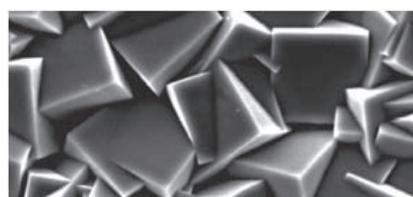


Highly Active Oxide Photocathode for Photoelectrochemical Water Reduction

A. Paracchino, V. Laporte, K. Sivula, M. Grätzel, E. Thimsen*, *Nat. Mater.* **2011**, *10*, 456

EPFL Lausanne

Photoelectrical water splitting by means of solar energy is an ideal method for the renewable production of hydrogen. Considering the large surfaces required, the semiconductors employed should be easy and cheap to manufacture. Cuprous oxide fulfills various requirements, but the use as a photocathode suffers from its poor stability in aqueous solutions. This latter issue was addressed by depositing protective layers of Al-doped ZnO and TiO₂ on the electrode surface by atomic layer deposition. Photocurrents of up to -7.6 mA cm^{-2} at a potential of 0 V versus the reversible hydrogen electrode at mild pH could be achieved and the electrodes remained active after 1 hour of testing. The Faradaic efficiency is estimated to be close to 100%.



Prepared by N. Bruns, V. Köhler, R. Kramer, P. Mauleón, F. Monnard and T. R. Ward

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Please contact thomas.ward@unibas.ch