



Swiss Science Concentrates

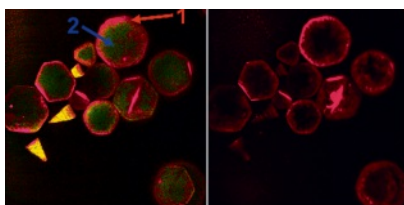
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Decorating the Edges of a 2D Polymer with a Fluorescence Label

Y. Zhao, R. H. M. Bernitzky, M. J. Kory, G. Hofer, J. Hofkens, and A. D. Schlüter*, *J. Am. Chem. Soc.* **2016**, *138*, 8976. ETH Zürich

2D polymers and other 2D materials exhibit properties that are different from common 3D materials. Despite their attractiveness as functional materials, the synthesis and further functionalization of 2D polymers remains challenging. In this publication, Schlüter and coworkers describe the preparation of edge-modified 2D polymers. Single crystals consisting of layered stacks of a 2D polymer with surface-exposed anthracenes are reacted with various substituted maleimide dienophiles. Micromechanical exfoliation of BODIPY-modified crystals results in thin, fluorescent sheet packages.

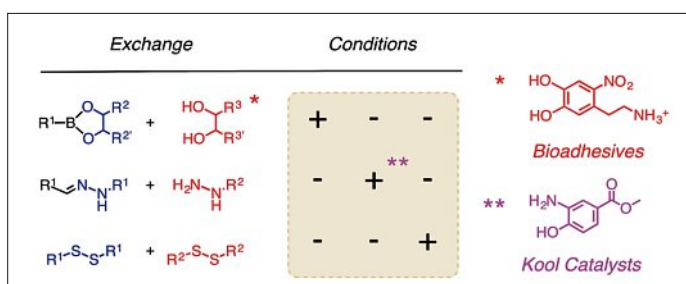


This work establishes the chemical nature of the edge groups of a 2D polymer and is the first implementation of an edge group modification.

The Third Orthogonal Dynamic Covalent Bond

S. Lascano, K.-D. Zhang, R. Wehlauch, K. Gademann, N. Sakai, and S. Matile*, *Chem. Sci.* **2016**, *7*, 4720. University of Geneva

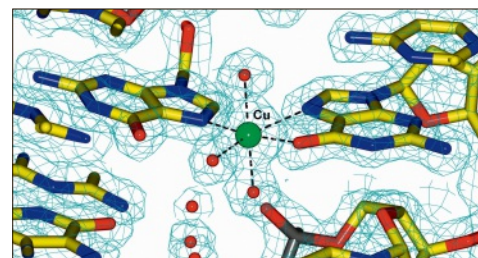
Depending on the conditions, dynamic covalent bonds behave either as inert or as rapidly exchanging bonds. For the construction of functional systems, multiple orthogonal types of dynamic covalent bonds are of great interest. The orthogonality of disulfides and hydrazones is well established. The application of boronate esters as the third bond, however, has failed so far due to incompatibility with hydrazone exchange conditions. Matile and coworkers now report the first functional system that operates with three fully orthogonal, organic dynamic covalent bonds. The authors screened a collection of bioinspired catechols with phenylboronic acids with vicinal substituents such as alcohols (benzoboroxoles), amines and fluorines for the most promising boronate esters. They identified conditions to selectively exchange disulfides, hydrazones and boronate esters. The results are important for future developments in the construction of dynamic functional systems.



N,N,O and N,O,N Meridional *cis* Coordination of Two Guanines to Copper(II) by d(CGCGCG)₂

M. Rohner, A. Medina-Molner, and B. Spingler*, *Inorg. Chem.* **2016**, *55*, 6130. University of Zurich

Linking modified or unmodified DNA building blocks with metals to generate supramolecular n-dimensional arrays is actively pursued. The use of natural nucleobases would avoid a potentially difficult synthesis, however, they have the disadvantage of a less defined metal coordination mode. Spingler and coworkers now describe the co-crystallization of copper(II) complexes with Z-DNA formed by unmodified hexamers d(CG)₃. Depending on the crystallization conditions, three different packing modes were observed. Guanine forms an unprecedented intramolecular O6,N7-chelate with the copper ions. Furthermore, copper mediates the formation of supramolecular DNA arrays in the crystal lattices. The study highlights the importance of transition metal coordination to natural DNA bases and their influence on DNA structure.



Allosterically Regulated Phosphatase Activity from Peptide-PNA Conjugates Folded Through Hybridization

T. Machida, S. Dutt, and N. Winssinger*, *Angew. Chem. Int. Ed.* **2016**, *55*, 8595. University of Geneva

Catalysis in living systems is generally achieved by large proteins folding in three-dimensional structures, although only a few residues actively participate in enzymatic catalysis. In an attempt to identify mimics of enzymatic phosphate hydrolysis, Winssinger and coworkers prepared and screened a library of peptide-PNA (peptide nucleic acids) conjugates. The authors identified a conjugate that undergoes a dramatic gain of activity (>25-fold) for phosphate hydrolysis when folded into a hairpin loop through hybridization. The hybridization-enforced folding leads to a protein-like function with allosteric regulation. The methodology complements alternative library design or screening methods based on phage display and catalytic dendrimers.

