



The following Communications have been judged by at least two referees to be “very important papers” and will be published online at www.angewandte.org soon:

S.-Y. Moon, J.-S. Bae, E. Jeon, J.-W. Park*

Organic Sol-Gel Synthesis: Solution-Processable Microporous Organic Networks

K. Sasaki, H. Naohara, Y. Cai, Y. M. C. Liu, M. B. Vukmirovic, J. X. Wang, R. R. Adzic

Platinum-Monolayer-Protected Cores: High-Stability Electrocatalysts for Fuel-Cell Cathodes

T. J. Hebden, A. J. S. John, D. G. Gusev, W. Kaminsky, K. I. Goldberg, D. M. Heinekey*

Preparation of a Dihydrogen Complex of Cobalt

S. Sun, G. Zhang, D. Geng, Y. Chen, R. Li, M. Cai, X. Sun*

A New Highly Durable Platinum Nanocatalyst for PEM Fuel Cells: Multiarmed Starlike Nanowire Single Crystals

J. S. Chen, T. Zhu, C. M. Li, X. W. Lou*

Building Hematite Nanostructures Using Oriented Attachment

K. Breuker,* S. Brüscheiler, M. Tollinger

Electrostatic Stabilization of Native Protein Structure in the Gas Phase

J. Zeng, X. Xia, M. Rycenga, P. Henneghan, Q. Li, Y. Xia*

Successive Deposition of Silver on Silver Nanoplates: Lateral Versus Vertical Growth

M. Mastalerz,* M. W. Schneider, I. M. Oppel, O. Presly

A Salicylbisimine Cage Compound with a High Surface Area and Selective CO₂/CH₄ Adsorption

J. Ballmann, A. Yeo, B. O. Patrick, M. D. Fryzuk*

Carbon–Nitrogen Bond Formation by Reaction of 1,2-Cumulenes with a Ditantalum Complex That Contains a Side-On- and End-On-Bound Dinitrogen

S. Lee, I. Chataigner,* S. R. Piettre*

Facile Dearomatization of Nitrobenzene Derivatives and Other Nitroarenes with N-Benzyl Azomethine Ylide

F. Lockyear, M. A. Parkes, S. D. Price*

Fast and Efficient Fluorination of Small Molecules by SF₄²⁺

X. Zeng, H. Beckers,* H. Willner,* J. F. Stanton

Elusive Diazirine: N₂CO

Author Profile



“When I wake up I try to ask a pertinent question of the seminar speaker (quote from Jay Siegel; I can't top that). The most significant scientific advance of the last 100 years has been Einstein's discovery that time actually equals money ...”

This and more about K. Peter C. Vollhardt can be found on page 34.

K. Peter C. Vollhardt ————— 34–36

News



A. Fürstner



C. M. Niemeyer



W. F. van
Gunsteren



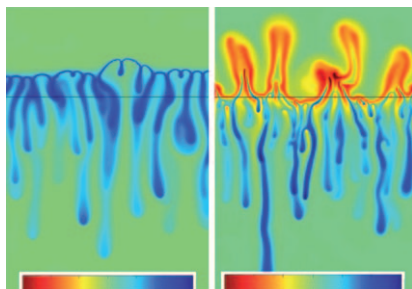
I. Willner



Y. Xia

New Members of the Editorial Board and the International Advisory Board: A. Fürstner, C. M. Niemeyer, W. F. van Gunsteren, I. Willner, and Y. Xia ————— 38–39

Highlights



Reactions that look after themselves:

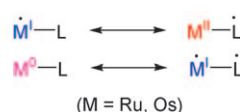
Interfacial instabilities caused by chemical reactions can increase the area of contact between fluids and enhance their mixing or dispersion. Although instabilities in macroscopic liquid/liquid systems are well-understood, “reactive mixing” at molecular length scales presents a challenge and an opportunity for future research. The picture shows two-dimensional density fields of two miscible reactive fluids.

Unstable Interfaces

B. A. Grzybowski* _____ 40–42

Reaction-Driven Mixing and Dispersion

Radical design: Unprecedented stability of ruthenium(I) and osmium(I) complexes with metalloradical character has been achieved by use of judiciously chosen supporting ligands based on the tris-(*o*-phosphinophenyl)silyl motif. The pronounced radical character on the ruthenium(I) center is also enforced by non-innocent ligands of the diiminopyridine type.

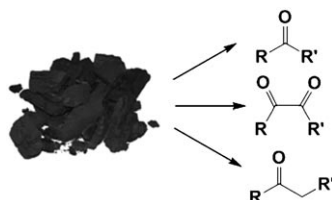


Metalloradicals

R. Poli* _____ 43–45

Ruthenium and Osmium Metalloradicals

More hip than nano: Bielawski and co-workers recently demonstrated the remarkable ability of graphene oxide to catalyze the oxidation of a variety of alcohols to the corresponding ketones/aldehydes, alkenes to the corresponding diones, and alkynes to the corresponding hydrates—a process they termed “carbocatalysis”. These efficient metal-free reactions mark a promising convergence of heterogeneous catalysis with graphene science.



Carbon Catalysts

J. Pyun* _____ 46–48

Graphene Oxide as Catalyst: Application of Carbon Materials beyond Nanotechnology

For the USA and Canada:

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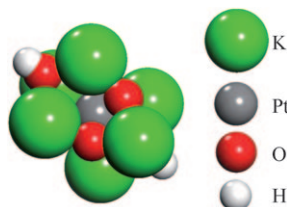
postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US\$ 9442/8583 (valid for print and electronic / print or electronic delivery); for

individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Heterogeneous Catalysis

J. M. Thomas* — 49–50

An Exceptionally Active Catalyst for Generating Hydrogen from Water



Rising to the challenge: A reliable, stable, safe, and low-cost method of producing H_2 from H_2O is needed so that this high-energy-density gas can serve as a cleaner source of energy, particularly for low-temperature fuel-cell-powered devices. An atomically dispersed Pt catalyst (see picture) recently developed on an inexpensive and inert support could well hold the key.

Essays

Hydrogen Bonds

G. R. Desiraju* — 52–59

A Bond by Any Other Name



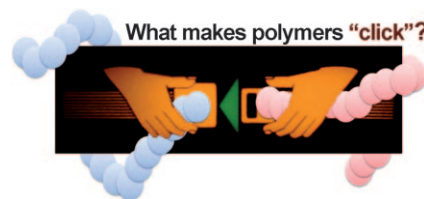
Speak not against my bond: Another definition of the hydrogen bond? Strong hydrogen bonds satisfy all current definitions of this phenomenon, but as weaker interactions $X-H \cdots Y-Z$ have been brought into the scope of hydrogen bonding, the definitions have had to change.

Polymer Click Reactions

C. Barner-Kowollik,* F. E. Du Prez,*
P. Espeel,* C. J. Hawker,* T. Junkers,*
H. Schlaad,* W. Van Camp* — 60–62

“Clicking” Polymers or Just Efficient Linking: What Is the Difference?

The “click” trick: Many reactions are classified as click reactions even though some are limited to certain applications. Thus, there is danger that the term “click” will become meaningless over time and simply a synonym for “successful”. To prevent this, the original click criteria are evaluated in this Essay specifically for the synthetic polymer field and a set of criteria are specified that distinguishes click from other efficient reactions.



Scientific Education

K. C. Nicolaou* — 63–74

Invigorating Education



Education, the mother of all progress, is the tool of choice to address today’s and tomorrow’s global problems. Reflecting on successes in the past, investment in research and education is discussed as the key to prosperity and our standard of living.

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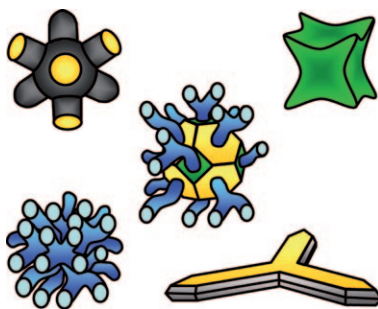
WILEY-VCH

Minireviews

Nanostructures

B. Lim, Y. Xia* — 76–85

Metal Nanocrystals with Highly Branched Morphologies

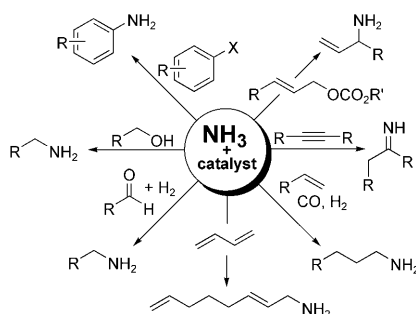


Branching out: Metal nanocrystals with highly branched morphologies, such as multipods and nanodendrites, have received growing attention owing to their unique structures and properties. The growth mechanisms, synthetic strategies, and potential applications for such branched metal nanocrystals are discussed.

Ammonia in Organic Synthesis

J. L. Klinkenberg, J. F. Hartwig* — 86–95

Catalytic Organometallic Reactions of Ammonia



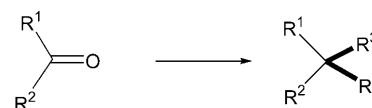
Get a move on ammonia: Reactions of ammonia catalyzed by transition-metal complexes allow direct access to primary amines and other nitrogen-containing functional groups. This Minireview presents recent advances in catalyst development that have led to the reaction of a variety of substrates with ammonia.

Geminal Disubstitution

D. Seebach* — 96–101

Generation of Secondary, Tertiary, and Quaternary Centers by Geminal Disubstitution of Carbonyl Oxygens

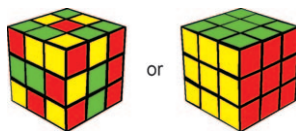
Two at a time: The replacement of the carbonyl oxygen atom in amides, lactams, aldehydes, ketones, and acid chlorides by two new substituents ($C=O \rightarrow CR^1R^2$) can be carried out with organometallic reagents (Li, Mg, Ti, Zr, Ce).



Dendrimer Synthesis

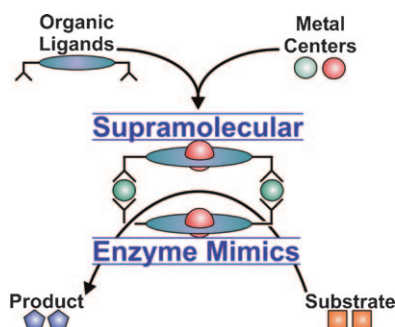
L. Röglin, E. H. M. Lempens,
E. W. Meijer* — 102–112

A Synthetic “Tour de Force”: Well-Defined Multivalent and Multimodal Dendritic Structures for Biomedical Applications



Statistically modified or well-defined?

This is an important question when studying multivalent probes for biomedical applications. The emergence of a variety of chemoselective conjugation reactions has allowed the synthesis of well-defined and monodisperse dendritic structures.



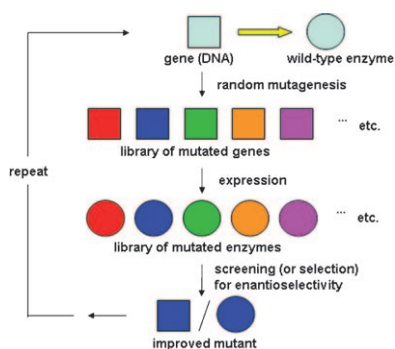
Not just copies: Recent advances in supramolecular coordination chemistry have allowed chemists to synthesize macromolecular complexes that exhibit various properties intrinsic to enzymes. This Review focuses on structures inspired by properties and functions observed in enzymes rather than precise models of enzyme active sites. Many of the structures exhibit reactivity and specificity reminiscent of natural systems, and some of them have functions that exceed the natural systems which provided the inspiration for initially making them.

Reviews

Enzyme Mimics

M. J. Wiester, P. A. Ulmann,
 C. A. Mirkin* 114–137

Enzyme Mimics Based Upon
 Supramolecular Coordination Chemistry



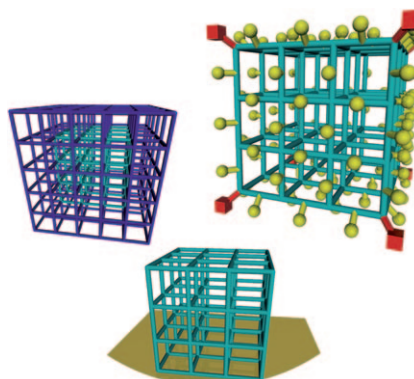
Evolution in the test tube: The traditional limitations of enzymes as catalysts in organic chemistry or biotechnology—comprising in many cases poor enantioselectivity, limited substrate scope, and insufficient stability—have been eliminated by the techniques of directed evolution. Iterative saturation mutagenesis in particular drives the efficient creation of a new generation of stereoselective biocatalysts which complement chiral synthetic homogeneous catalysts.

Protein Engineering

M. T. Reetz* 138–174

Laboratory Evolution of Stereoselective
 Enzymes: A Prolific Source of Catalysts for
 Asymmetric Reactions

MOFs on surfaces: Many parameters need to be considered in the formation of metal–organic frameworks (MOFs; see structures) at the liquid–solid interface. The methods and growth mechanisms for the layer-by-layer deposition of MOFs on functional materials, the homo- and heteroepitaxial deposition of MOF heterocrystals, and the coordination modulation of MOF surfaces are reviewed.



Metal–Organic Frameworks

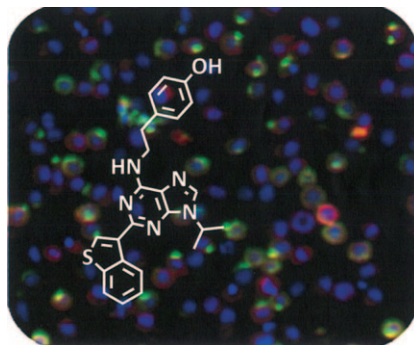
D. Zacher, R. Schmid, C. Wöll,
 R. A. Fischer* 176–199

Surface Chemistry of Metal–Organic
 Frameworks at the Liquid–Solid Interface

Regenerative Medicine

C. A. Lyssiotis,* L. L. Lairson,
A. E. Boitano, H. Wurdak, S. Zhu,
P. G. Schultz* — 200–242

Chemical Control of Stem Cell Fate and
Developmental Potential



Small molecules can be used as tools to control stem cell fate. These molecules have provided a wealth of insights into the signaling and epigenetic mechanisms that regulate stem cell biology and are beginning to contribute to the development of effective treatments for tissue repair and regeneration.

Communications

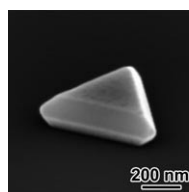


Nanostructures

J. Zeng, X. Xia, M. Rycenga,
P. Henneghan, Q. Li, Y. Xia* — 244–249



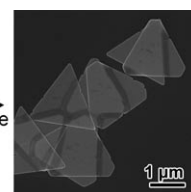
Successive Deposition of Silver on Silver
Nanoplates: Lateral versus Vertical
Growth



{100} capping
with PVP



{111} capping
with Sodium citrate



If the cap fits: The epitaxial growth of Ag on Ag nanoplates could be directed to preferentially occur along the lateral or vertical direction by using sodium citrate or poly(vinyl pyrrolidone) (PVP) as capping agents (see picture). The edge length

and thickness of the Ag nanoplates could be increased by 100 and 40 times, respectively. Raman scattering signals of Ag nanospheres on the Ag nanoplates were enhanced as the nanoplates became thicker.

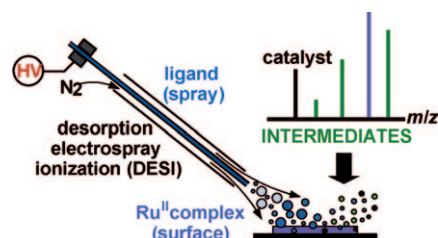
Mass Spectrometry

R. H. Perry, M. Splendore, A. Chien,
N. K. Davis, R. N. Zare* — 250–254



Detecting Reaction Intermediates in
Liquids on the Millisecond Time Scale
Using Desorption Electrospray Ionization

Capturing transient species: The bombardment of a surface-bound Ru^{II} complex with charged droplets containing a ligand allows the detection of reaction intermediates (see figure). The reaction investigated is used to synthesize Ru^{II} catalysts containing amino alcohol ligands, which facilitate the asymmetric transfer hydrogenation of ketones and imines.



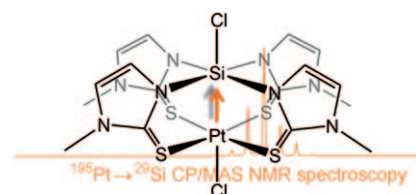
Heavy-Atom Effect

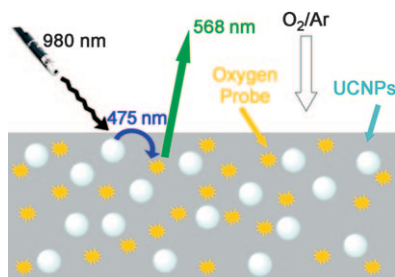
L. A. Truflandier, E. Brendler, J. Wagler,*
J. Autschbach* — 255–259



²⁹Si DFT/NMR Observation of Spin–Orbit
Effect in Metallasilatrane Sheds Some
Light on the Strength of the Metal→
Silicon Interaction

SO what? Spectral features caused by relativistic effects on chemical shift tensors are not always looked for in solid-state NMR spectroscopy. Slow-rotation ²⁹Si magic-angle spinning (MAS) NMR measurements on the triad [ClTM(μ-mt)₂SiCl] (TM = Pt, Pd, Ni; mt = 2-mercapto-1-methylimidazole) reveal that heavy-atom spin–orbit (SO) coupling has a dramatic impact on the ²⁹Si NMR spectral peak shape.



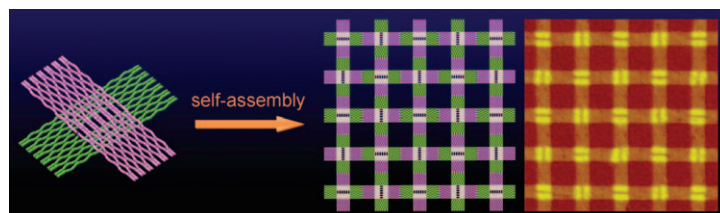


Turned off by oxygen: Luminescent upconverting nanoparticles (UCNPs) of the type $\text{NaYF}_4:\text{Yb},\text{Tm}$ are employed in an entirely new type of optical sensor for oxygen (see picture). Upon laser excitation at 980 nm, these UCNPs act as nanolamps, the blue emission of which is used to photoexcite an iridium complex dissolved in ethyl cellulose. Its green emission, in turn, is dynamically and fully reversibly quenched by molecular oxygen.

Oxygen Sensors

D. E. Achatz, R. J. Meier, L. H. Fischer, O. S. Wolfbeis* — 260–263

Luminescent Sensing of Oxygen Using a Quenchable Probe and Upconverting Nanoparticles



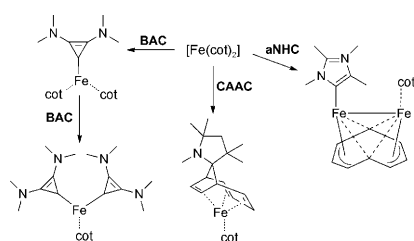
DNA origami gets large: A double-layer DNA-origami tile with two orthogonal domains underwent self-assembly into well-ordered two-dimensional DNA arrays with edge dimensions of 2–3 μm (see

schematic representation and AFM image). This size is likely to be large enough to connect bottom-up methods of patterning with top-down approaches.

DNA Nanotechnology

W. Liu, H. Zhong, R. Wang, N. C. Seeman* — 264–267

Crystalline Two-Dimensional DNA-Origami Arrays



Carbenes attack! Stable carbenes react with $[\text{Fe}(\text{cot})_2]$ in very different ways. Whereas the classical N-heterocyclic carbenes induce the formation of tetra- and trimetallic iron clusters, abnormal NHCs and carbocyclic carbenes (BACs) form mono- and bimetallic iron complexes. Cyclic (alkyl) (amino)carbenes (CAACs) react with $[\text{Fe}(\text{cot})_2]$ in a completely different manner, namely through outer-sphere $[4+1]$ cycloaddition.

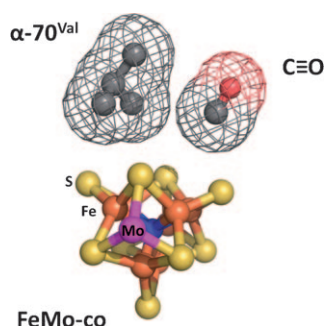
Iron–Carbene Interactions

V. Lavallo, A. El-Batta, G. Bertrand, R. H. Grubbs* — 268–271

Insights Into the Carbene-Initiated Aggregation of $[\text{Fe}(\text{cot})_2]$



Revealing kinetics: For the α -70 residue of MoFe nitrogenase in *Azotobacter vinelandii* the impact of substitution on the CO coordination to the enzyme's active center was studied by using stopped-flow IR spectroscopy. The results suggest that in all cases the CO ligand binds to the Fe 2-3-6-7 face of the FeMo-cofactor (see picture).



Nitrogenase

Z.-Y. Yang, L. C. Seefeldt, D. R. Dean, S. P. Cramer, S. J. George* — 272–275

Steric Control of the Hi-CO MoFe Nitrogenase Complex Revealed by Stopped-Flow Infrared Spectroscopy

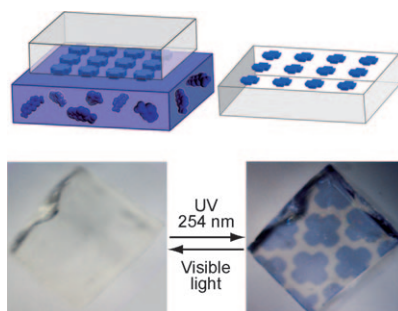


Micropatterning

S. Han, Y. Wei, C. Valente, R. S. Forgan, J. J. Gassensmith, R. A. Smaldone, H. Nakanishi, A. Coskun, J. F. Stoddart, B. A. Grzybowski* **276–279**



Imprinting Chemical and Responsive Micropatterns into Metal–Organic Frameworks

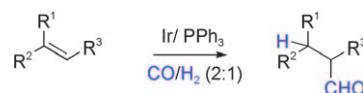


Stamp of approval: Wet stamping allows metal–organic framework (MOF) crystals to be imprinted with micropatterns of various organic chemicals. Printing the MOFs with photochromic molecules and pH indicators generates stimuli-responsive micropatterns which change their appearance upon contact with specific chemicals (see picture), thus reporting the environmental “status” of the crystal.

Hydroformylation

I. Piras, R. Jennerjahn, R. Jackstell, A. Spannenberg, R. Franke, M. Beller* **280–284**

A General and Efficient Iridium-Catalyzed Hydroformylation of Olefins



Breaking with conventional wisdom: Hydroformylation catalysts are generally based on rhodium; earlier, cobalt was used. Iridium, which is less expensive than rhodium, was considered too unreactive. However, iridium/phosphine

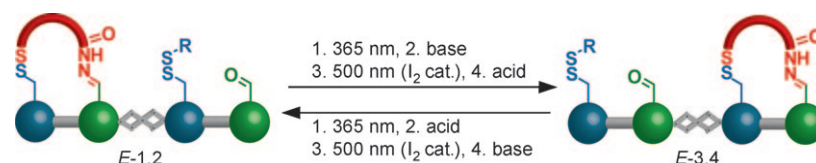
complexes have now been shown to form active catalysts for the hydroformylation of olefins under mild conditions (see scheme; R¹, R² = H, alkyl, aryl; R³ = H, alkyl). Competing hydrogenation side reactions can be suppressed.

Molecular Devices

M. J. Barrell, A. G. Campaña, M. von Delius, E. M. Geertsema, D. A. Leigh* **285–290**



Light-Driven Transport of a Molecular Walker in Either Direction along a Molecular Track



Walk this way! A walker unit is able to walk in either direction along a four-foothold molecular track, depending on the sequence of application of four external stimuli: acid, base, UV light, and visible

light in the presence of iodine (see picture). The isomerization of the stilbene moiety in the molecular track is key for the achievement of directional transport through a Brownian ratchet mechanism.

Dyes/Pigments

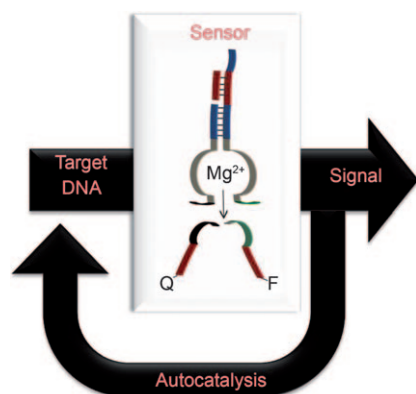
R. O. MacRae, C. M. Pask, L. K. Burdsall, R. S. Blackburn, C. M. Rayner, P. C. McGowan* **291–294**



The Combined Synthesis and Coloration of Poly(lactic acid)



True colors: A catalytic process that allows color to be integrated directly into poly(lactic acid) eliminates the need for subsequent wet-processing operations. The technical performance of the new polymers is superior to that of conventionally dyed substrates and the polymers are significantly more sustainable for applications in the textiles industry (see picture) in terms of environmental impact and economics of the coloration process.

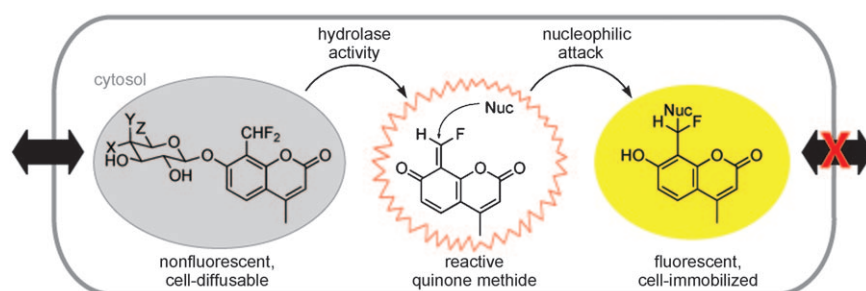


Sense and sensibility: Amplified DNA detection is accomplished by the autocatalytic cleavage of a programmed nucleic acid structure based on the Mg^{2+} -dependent DNAzyme E6 (see picture). The analyte sequence is autocatalytically generated by the DNAzyme from a reporter nucleic acid, which is labeled with a fluorophore and quencher at its two ends.

Autocatalysis

F. Wang, J. Elbaz, C. Teller, I. Willner* 295–299

Amplified Detection of DNA through an Autocatalytic and Catabolic DNAzyme-Mediated Process



Fluorescence Imaging

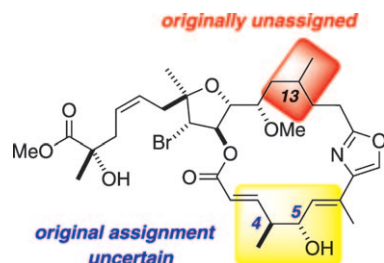
D. H. Kwan, H.-M. Chen, K. Ratananikom, S. M. Hancock, Y. Watanabe, P. T. Kongsaree, A. L. Samuels, S. G. Withers* 300–303

Self-Immobilizing Fluorogenic Imaging Agents of Enzyme Activity



Lighting up enzyme activity: Fluorogenic enzyme substrates have been developed that upon hydrolysis form reactive quinone methides, which can react with cell components in vivo to generate an

immobilized fluorescent label (see scheme). These compounds can be used for the histological staining of tissues or activity-based screening of cells by fluorescence-activated cell sorting.



Out of options? Even though a systematic approach was chosen, which led to a set of four diastereomeric macrolides modeled around the proposed structure of leiodolide B (see picture), the puzzle concerning the stereostructure of this cytotoxic metabolite derived from a deep-sea sponge still remains unsolved.

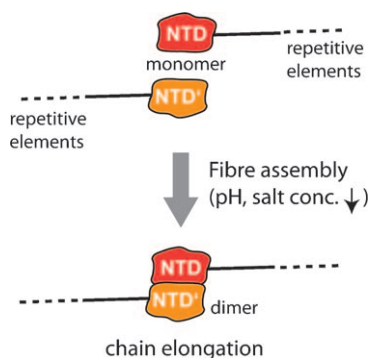
Natural Product Synthesis

A. Larivée, J. B. Unger, M. Thomas, C. Wirtz, C. Dubost, S. Handa, A. Fürstner* 304–309

The Leiodolide B Puzzle



One of the toughest protein fibers: The N-terminal domain (NTD) of spider dragline silk shows a pH-dependent monomer–dimer equilibrium: The N-terminal domain silk protein is stored as a stabilized monomer at neutral pH and high salt concentration, whereas during fiber assembly at a lower pH value this domain is able to form antiparallel dimers. Multivalent linking results in endless and highly stable fibers (see picture).



Spider Silk

F. Hagn, C. Thamm, T. Scheibel, H. Kessler* 310–313

pH-Dependent Dimerization and Salt-Dependent Stabilization of the N-terminal Domain of Spider Dragline Silk—Implications for Fiber Formation

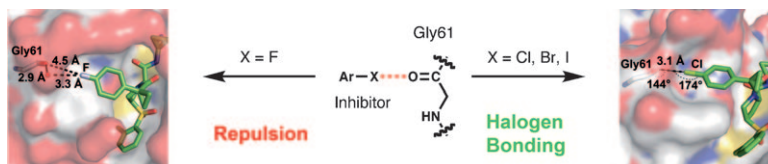


Halogen Bonding

L. A. Hardegger, B. Kuhn, B. Spinnler, L. Anselm, R. Ecabert, M. Stihle, B. Gsell, R. Thoma, J. Diez, J. Benz, J.-M. Plancher, G. Hartmann, D. W. Banner,* W. Haap,* F. Diederich* _____ 314–318



Systematic Investigation of Halogen Bonding in Protein–Ligand Interactions



Halogen bonding triggers activity:

Increasing binding affinity was observed for a series of covalent human Cathepsin L inhibitors by exchanging an aryl ring H atom with Cl, Br, and I, which undergo halogen bonding with the C=O

group of Gly61 in the S3 pocket of the enzyme. Fluorine, in contrast, strongly avoids halogen bonding (see scheme). The strong distance and angle dependence of halogen bonding was confirmed for biological systems.



Supporting information is available on www.angewandte.org (see article for access details).



A video clip is available as Supporting Information on www.angewandte.org (see article for access details).



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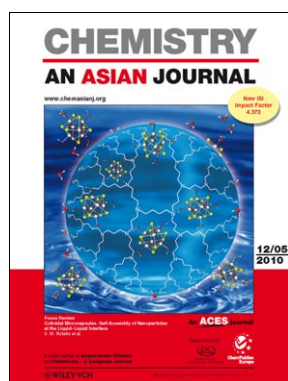
Spotlight on Angewandte's Sister Journals _____ 30–32

Notice to Authors _____ 319

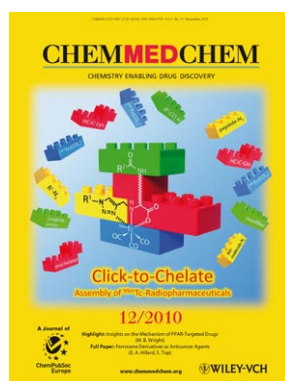
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The issues for December 2010 appeared online on the following dates
Issue 49: December 1 • Issue 50: December 7 • Issue 51: December 14 • Issue 52: December 17

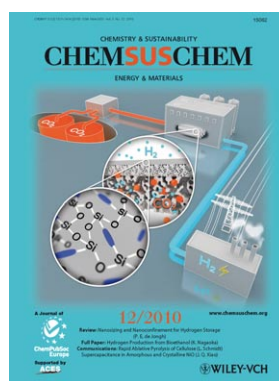
Check out these journals:



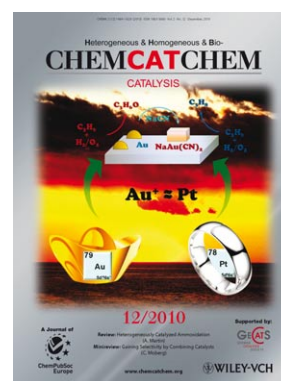
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