



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:

J. Zhang, X.-J. Wu, Z. Wang, Y. Chen, X. Wang, M. Zhou, H. Scheer, K. Zhao*

Single Fused Gene Approach to Photoswitchable and Fluorescent Biliproteins

Y. Sohma,* Q. Hua, J. Whittaker, M. A. Weiss, S. B. H. Kent*
Design and Folding of [GluA4(OβThrB30)]Insulin (Ester Insulin), a Minimal Proinsulin Surrogate Chemically Convertible into Human Insulin

A. C. Stelzer, J. D. Kratz, Q. Zhang, H. M. Al-Hashimi*
RNA Dynamics by Design: Biasing Ensemble towards Ligand Bound States

T. Ikawa, A. Takagi, Y. Kurita, K. Saito, K. Azechi, M. Egi, K. Kakiguchi, Y. Kita, S. Akai*
Preparation of Borylbenzynes and their Use in the Regioselective Diels–Alder Reaction: Synthesis of Functionalized Arylboronates

Z. Zhang, Z. Wang, R. Zhang, K. Ding*

Extremely Efficient Titanium Catalyst for the Enantioselective Cyanation of Aldehydes Using Cooperative Catalysis

Q. Wang, M. Zhang, C. Chen, W. Ma, J. Zhao*
Photocatalytic Aerobic Oxidation of Alcohols on TiO₂: The Acceleration Effect of Brønsted Acids

Y. Fu, Q. Dai, W. Zhang, J. Ren, T. Pan,* C. He*
AlkB Domain of Mammalian ABH8 Catalyzes Hydroxylation of 5-Methoxycarbonylmethyluridine at the Wobble Position of tRNA

H. Braunschweig,* K. Radacki, A. Schneider
Cyclodimerization of an Oxoboryl Complex Induced by trans-Ligand Abstraction



“My favorite subjects at school were natural sciences, history, music lessons, and the theatre group. The biggest challenge facing scientists is solving social challenges with the achievements of scientific knowledge ...”

This and more about Roderich D. Süssmuth can be found on page 5032.

Author Profile

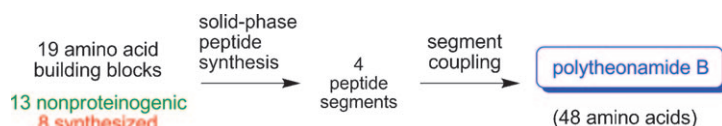
Roderich D. Süssmuth _____ 5032

Handbook of Synthetic Photochemistry

Angelo Albini, Maurizio Fagnoni

Books

reviewed by A. G. Griesbeck _____ 5033



Beyond the ribosome: The highly cytotoxic 48-residue nonribosomal peptide polytheonamide B, proposed to act as an ion channel, was synthesized by the coupling of four building blocks. The assembly of these peptide segments required the syn-

thesis of eight nonproteinogenic amino acids, including a unique sulfoxide. This first synthetic route towards polytheonamide B (see scheme) demonstrates the potential of state-of-the-art peptide chemistry.

Highlights

Natural Products

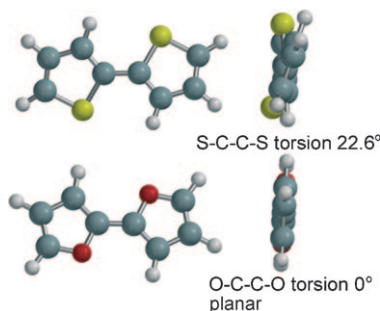
C. Ducho* _____ 5034–5036

Convergence Leads to Success: Total Synthesis of the Complex Nonribosomal Peptide Polytheonamide B

α -Oligofurans

U. H. F. Bunz* — 5037 – 5040

α -Oligofurans: Molecules without a Twist



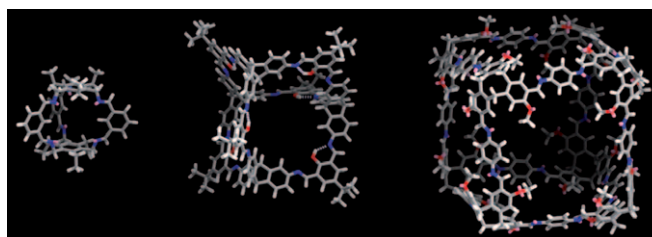
Be planar! The planar oligofurans (see picture, lower; C gray, H white, O red) are, despite a lack of solubilizing alkyl groups, quite soluble. They are also highly fluorescent and surprisingly stable, and might give the oligothiophenes (upper; S yellow) a run for their money when seeking applications in organic electronics.

Minireviews

Cage Compounds

M. Mastalerz* — 5042 – 5053

Shape-Persistent Organic Cage Compounds by Dynamic Covalent Bond Formation



Hole in one: Discrete organic molecules with defined cavities are accessible in one synthetic step by reversible reactions (e.g. Schiff base or boronic ester condensations). This Minireview highlights recent progress in the synthesis of organic cage

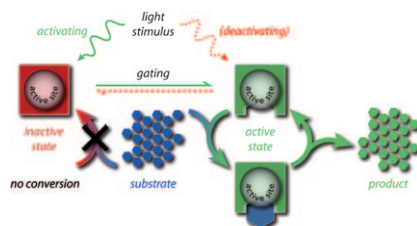
compounds by dynamic covalent chemistry. The picture shows three cage molecules of various size, synthesized by [3+2], [6+4], and [8+12] imine condensation reactions.

Reviews

Photochemistry

R. S. Stoll, S. Hecht* — 5054 – 5075

Artificial Light-Gated Catalyst Systems



Plug-and-play catalysis: An active catalyst system enabled by switching on light allows a specific chemical transformation at well-defined location and time, thanks to the high spatial and temporal resolution of the initial light stimulus. Such artificial light-gated systems can be specifically designed for particular applications.

For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals

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

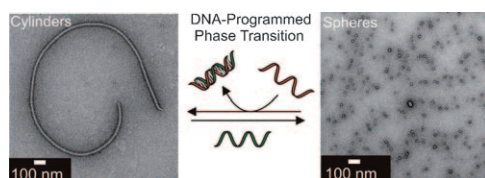
individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Communications

DNA Nanotechnology

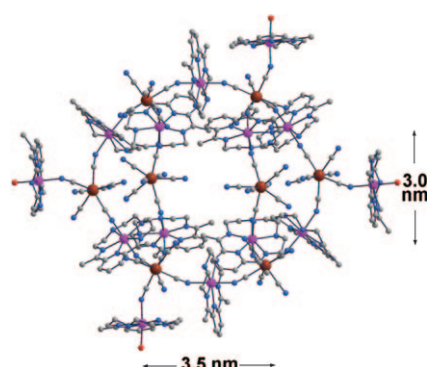
M.-P. Chien, A. M. Rush,
M. P. Thompson,
N. C. Gianneschi* _____ 5076–5080

Programmable Shape-Shifting Micelles



Getting in shape: DNA-brush copolymer amphiphiles assemble into micelles with morphologies determined by selective interactions that allow manipulation of the magnitude of steric and electrostatic

repulsions in the micelle shells. Cylinder-to-sphere phase transitions occur when an input DNA sequence is added to the micelles (see picture).



I'll take the high road: An anionic nano-size dicosanuclear $\{\text{Mo}_8\text{Mn}_{14}\}$ cluster based on the $[\text{Mo}(\text{CN})_7]^{4-}$ unit was synthesized and fully characterized by X-ray and magnetic studies. This molecule (see picture; Mo red, Mn purple, C gray, N blue) is the first discrete compound based on $[\text{Mo}(\text{CN})_7]^{4-}$ and contains the most paramagnetic centers (22) and the largest ground state spin value ($S=31$) for a cyanide-bridged cluster.

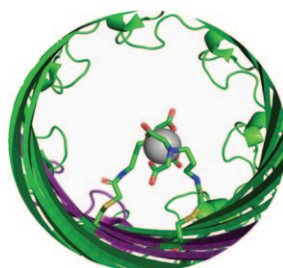
Magnetic Properties

X. Y. Wang, A. V. Prosvirin,
K. R. Dunbar* _____ 5081–5084

A Dicosanuclear $\{\text{Mo}_8\text{Mn}_{14}\}$ Cluster
Based on $[\text{Mo}(\text{CN})_7]^{4-}$



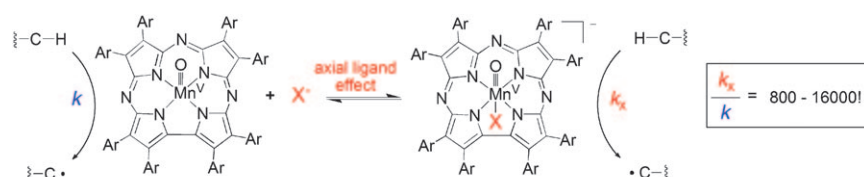
A double hug: Two half-chelating ligands were covalently attached within the lumen of a protein nanopore (see picture). By electrical recording, the formation of fully chelated Zn^{2+} ions was monitored at the single-molecule level, thus revealing the rate constants for the eight major steps in the process.



Metal-Ion Chelation

A. F. Hammerstein, S.-H. Shin,
H. Bayley* _____ 5085–5090

Single-Molecule Kinetics of Two-Step
Divalent Cation Chelation



Runaway reactivity: A manganese(V)-oxo porphyrinoid complex displays an unprecedented increase in reaction rate for a hydrogen-atom abstraction upon addition of anionic axial ligands ($\text{X} = \text{F}^-$ and CN^- ;

see scheme). Density functional theory calculations are in excellent agreement with experiment, and provide insight into the origins of these remarkable axial ligand effects.

Biomimetic Chemistry

K. A. Prokop, S. P. de Visser,*
D. P. Goldberg* _____ 5091–5095

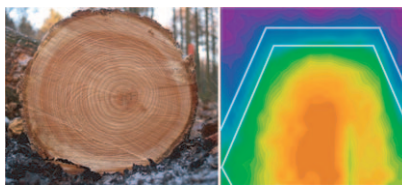
Unprecedented Rate Enhancements of
Hydrogen-Atom Transfer to a
Manganese(V)-Oxo Corrolazine Complex



Crystal Growth

B. A. Palmer, K. D. M. Harris,*
F. Guillaume* 5096–5100

A Strategy for Retrospectively Mapping the Growth History of a Crystal



Like the rings of a tree: A novel strategy is presented that yields insights on crystal growth processes from retrospective analysis of crystals recovered at the end of the process. The strategy is based on systems in which the composition of the growing crystal surfaces varies during crystal growth, while the crystal structure remains constant. The compositional distribution in the crystal is monitored using confocal Raman microspectrometry (see picture).

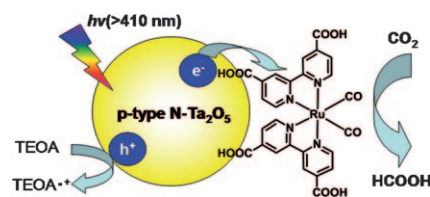
Photocatalysis

S. Sato,* T. Morikawa, S. Saeki, T. Kajino,
T. Motohiro 5101–5105



Visible-Light-Induced Selective CO₂ Reduction Utilizing a Ruthenium Complex Electrocatalyst Linked to a p-Type Nitrogen-Doped Ta₂O₅ Semiconductor

Lights, CO₂, action! Selective CO₂ reduction by hybrid photocatalysts such as a p-type semiconductor and a ruthenium complex catalyst (see picture) was induced by visible light. The quantum efficiency for HCOOH production was 1.9% at 405 nm. For electron transfer, it is essential that the potential of the conduction band minimum of the semiconductor is more negative than the reduction potential of the complex catalyst.

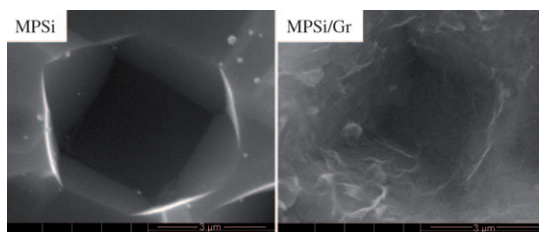


Photoconversion

H. T. Yu, S. Chen, X. F. Fan, X. Quan,*
H. M. Zhao, X. Y. Li,
Y. B. Zhang 5106–5109

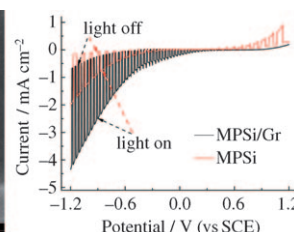


A Structured Macroporous Silicon/Graphene Heterojunction for Efficient Photoconversion



New roles of graphene as a protective layer and transparent charge collector are demonstrated in a structured macroporous Si (MPSi)/graphene (Gr) hetero-

junction, which shows stable photocurrent (see picture) and a maximum photoconversion efficiency of 2.36% in 0.05 M H₂SO₄ without adding a redox pair.

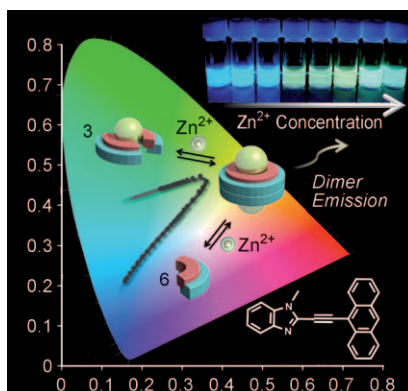


Supramolecular Chemistry

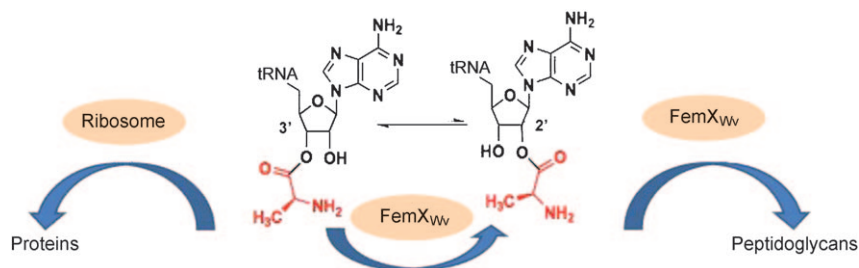
T. Ogawa, J. Yuasa,*
T. Kawai* 5110–5114



Highly Selective Ratiometric Emission Color Change by Zinc-Assisted Self-Assembly Processes



Color sense: 2-(Anthracen-9-ylethynyl)-1-methylbenzimidazole (BzIm-An) shows a ratiometric color change in emission from blue to light yellow to green with increasing Zn²⁺ concentration. The dimeric 3:1 complex [(BzIm-An)₃Zn²⁺]₂ formed at low Zn²⁺ concentration is converted into the 2:1 complex [(BzIm-An)₂Zn²⁺] at high concentrations of Zn²⁺.



Natural selection: Replacement of the 3'-OH group of Ala-tRNA^{Ala} with 3'-H affected FemX_{WW}-catalyzed aminoacyl transfer from the 2'-position, but not substrate binding. The ability of FemX_{WW}

to bind and transacylate the 3'-O-Ala isomer initially formed by alanyl-tRNA synthetase (AlaRS) may be crucial for efficient competition with the ribosome (see scheme).

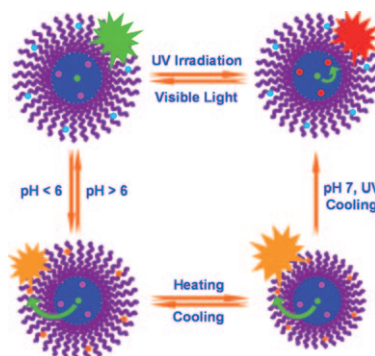
Aminoacyl-tRNA Mimics

M. Fonvielle, M. Chemama, M. Lecerf, R. Villet, P. Busca, A. Bouhss, M. Ethève-Quellejeu,*
M. Arthur* ————— 5115–5119

Decoding the Logic of the tRNA Regiospecificity of Nonribosomal FemX_{WW} Aminoacyl Transferase



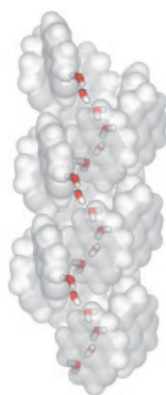
Micellar traffic lights: The title FRET system (FRET = fluorescence resonance energy transfer) consists of one type of donor dye and two types of acceptor dyes. On/off fluorescence switching of the latter two dyes can be controlled by pH changes and light, respectively. This novel type of multicolor luminescent polymeric assembly can act as a ratiometric probe for pH and temperature with tunable sensitivity.



Luminescent Probes

C. Li, Y. Zhang, J. Hu, J. Cheng,*
S. Liu* ————— 5120–5124

Reversible Three-State Switching of Multicolor Fluorescence Emission by Multiple Stimuli Modulated FRET Processes within Thermoresponsive Polymeric Micelles

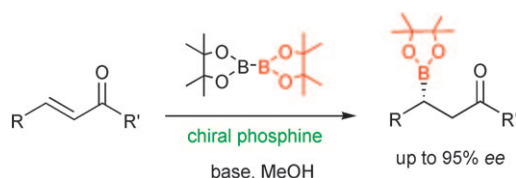


Pore design: Nanoporous steroidal crystals can be engineered for a range of channel properties. For example, the walls may be coated with aromatic groups to mimic the interior of carbon nanotubes (CNTs). The pores in these structures are occupied by “water wires”, as proposed for water in CNTs themselves.

Water Wires

R. Natarajan, J. P. H. Charmant, A. G. Orpen, A. P. Davis* — 5125–5129

Water Chains in Hydrophobic Crystal Channels: Nanoporous Materials as Supramolecular Analogues of Carbon Nanotubes



Enantiomerically enriched secondary organoboronates containing β -carbonyl functional groups have been prepared using an unprecedented organocatalytic

system (see scheme). The use of chiral tertiary phosphorus compounds induced *ee* values of up to 95% in the absence of transition metals.

Organocatalysis

A. Bonet, H. Gulyás,*
E. Fernández* ————— 5130–5134

Metal-Free Catalytic Boration at the β -Position of α,β -Unsaturated Compounds: A Challenging Asymmetric Induction



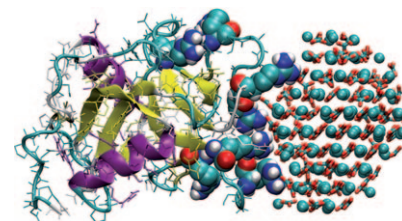
Biomaterialization

C. L. Freeman, J. H. Harding, D. Quigley,
P. M. Rodger* 5135–5137



Structural Control of Crystal Nuclei by an
Eggshell Protein

Growing a good egg: Metadynamics simulations show that the eggshell protein ovocleidin-17 induces the formation of calcite crystals from amorphous calcium carbonate nanoparticles. Multiple spontaneous crystallization and amorphization events were simulated; these simulations suggest a catalytic cycle that explains the role of ovocleidin-17 in the first stages of eggshell formation (the picture shows one intermediate of this cycle).

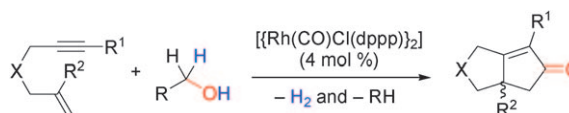


Pauson–Khand Reaction

J. H. Park, Y. Cho,
Y. K. Chung* 5138–5141



Rhodium-Catalyzed Pauson–Khand-Type
Reaction Using Alcohol as a Source of
Carbon Monoxide



Three in one pot! Bicyclic cyclopentenones have been synthesized from enynes in alcohol in the presence of a rhodium catalyst through a newly developed auto-tandem catalytic reaction. This process combines three mechanistically

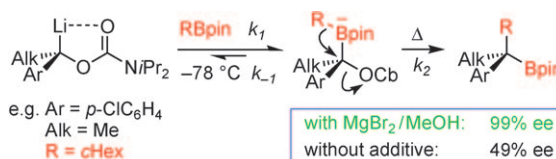
distinctive reactions—an oxidation of alcohols, a decarbonylation of aldehydes, and a carbonylative [2+2+1] cycloaddition (see scheme; dppp = propane-1,3-diylbis(diphenylphosphane)).

Enantioselective Synthesis

V. Bagutski, R. M. French,
V. K. Aggarwal* 5142–5145



Full Chirality Transfer in the Conversion of
Secondary Alcohols into Tertiary Boronic
Esters and Alcohols Using Lithiation–
Borylation Reactions



New conditions, full transfer: Using $\text{MgBr}_2/\text{MeOH}$ as an additive now provides essentially 100% retention of configuration in the lithiation–borylation reaction, thus leading to tertiary boronic esters (or tertiary alcohols) with excep-

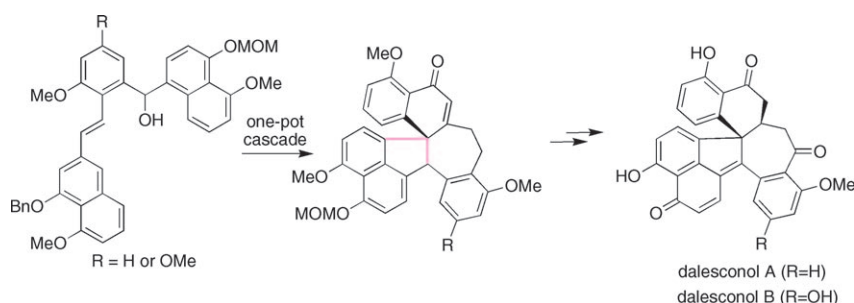
tionally high *ee* values in all cases—even with rather hindered substrates and more stabilized lithiated carbamates (see scheme; Cb = carbamate, pin = $\text{OCMe}_2\text{CMe}_2\text{O}$).

Natural Products

S. A. Snyder,* T. C. Sherwood,
A. G. Ross 5146–5150

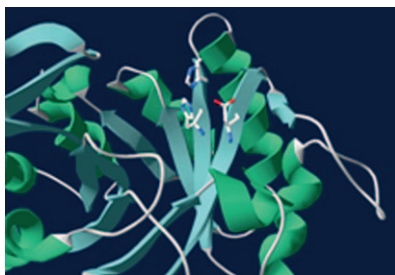


Total Syntheses of Dalesconol A and B



A polycyclic collapse: Use of a carefully designed acyclic intermediate participated in a cascade reaction that formed the entire core of the polyketide-derived dalesconols in a single flask (see scheme).

A number of additional and carefully controlled synthetic operations completed an expeditious synthesis of both of these highly bioactive natural products as well as structural congeners.

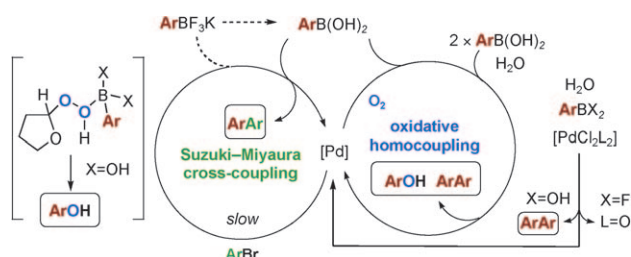


Guided by nature: A designed binding site comprising the His/His/Asp motif for Cu^{II} complexation has been constructed in a robust protein by site-specific mutagenesis (see picture). The artificial metalloenzyme catalyzes an enantioselective Diels–Alder reaction.

Artificial Metalloenzymes

J. Podtetenieff, A. Taglieber, E. Bill, E. J. Reijerse, M. T. Reetz* — **5151–5155**

An Artificial Metalloenzyme: Creation of a Designed Copper Binding Site in a Thermostable Protein



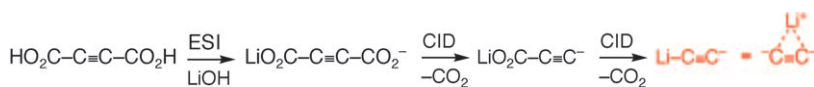
Undercover agents: The biaryl coupling of an aryltrifluoroborate with an aryl bromide involves in situ hydrolysis of the boron reagent. The hydrolysis products are key components in ensuring that the reaction

proceeds with high efficiency and avoids the extensive generation of undesired phenolic and homocoupling side products.

Reaction Mechanisms

M. Butters, J. N. Harvey, J. Jover, A. J. J. Lennox, G. C. Lloyd-Jones,* P. M. Murray — **5156–5160**

Aryl Trifluoroborates in Suzuki–Miyaura Coupling: The Roles of Endogenous Aryl Boronic Acid and Fluoride



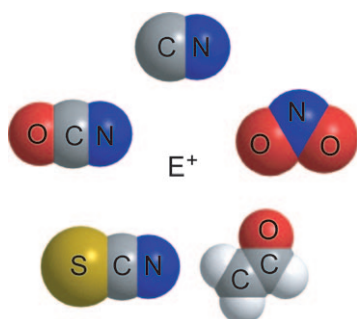
No solvent, no complications! The lithium acetylide ion, which is the monolithium salt of the carbide ion, was prepared in the gas phase (see scheme; CID = collision-

induced dissociation, ESI = electrospray ionization). Its reactivity and energetics are reported along with high-level computational results.

Gas-Phase Synthesis

M. M. Meyer, B. Chan, L. Radom, S. R. Kass* — **5161–5164**

Gas-Phase Synthesis and Reactivity of Lithium Acetylide Ion, Li–C≡C[−]



A better approach to ambident reactivity: The principle of hard and soft acids and bases (HSAB) cannot rationalize the reactivities of even the prototypical ambident nucleophiles shown in the picture. Marcus theory, which describes activation energies by a combination of intrinsic and thermodynamic terms, is a superior alternative.

Ambident Nucleophiles

M. Breugst, H. Zipse, J. P. Guthrie, H. Mayr* — **5165–5169**

Marcus Analysis of Ambident Reactivity



Protein Labeling

W. Peters, S. Willnow, M. Duisken,
H. Kleine, T. Macherey, K. E. Duncan,
D. W. Litchfield, B. Lüscher,
E. Weinhold* ————— 5170–5173



Enzymatic Site-Specific Functionalization
of Protein Methyltransferase Substrates
with Alkynes for Click Labeling



Pass and click: Protein methylation is an important posttranslational modification. Because the methyl group is a poor reporter group, new methods are needed to analyze methyltransferase substrates. A *S*-adenosyl-L-methionine-based cofactor

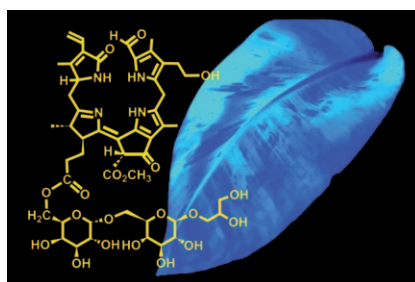
was synthesized and used for the site-specific functionalization of proteins with alkynes by methyltransferases (first step) and subsequent labeling through CuAAC click chemistry (second step; see scheme).

Blue Luminescent Leaves

S. Banala, S. Moser, T. Müller, C. Kreutz,
A. Holzinger, C. Lütz,
B. Kräutler* ————— 5174–5177



Hypermodified Fluorescent Chlorophyll
Catabolites: Source of Blue Luminescence
in Senescent Leaves



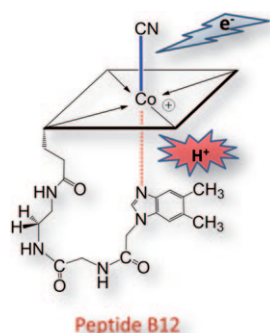
Yellow leaves of bananas glow blue under UV light. The luminescence is caused by uniquely glycosylated (“hypermodified”) chlorophyll catabolites that accumulate in senescent banana leaves. These findings suggest that (some) chlorophyll catabolites are not mere detoxification products, but are likely to play still unknown physiological roles.

Biomimetics

K. Zhou, F. Zelder* ————— 5178–5180



Vitamin B₁₂ Mimics Having a Peptide
Backbone and Tuneable Coordination and
Redox Properties



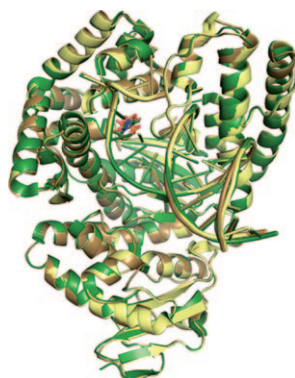
A fortified vitamin: A new class of vitamin B₁₂ mimics with a peptide backbone has been developed (see structure). The choice of an appropriate linker between the corrin macrocycle and the dimethylbenzimidazole base makes it possible to modulate selectively the coordination and redox properties at the metal center.

DNA Replication

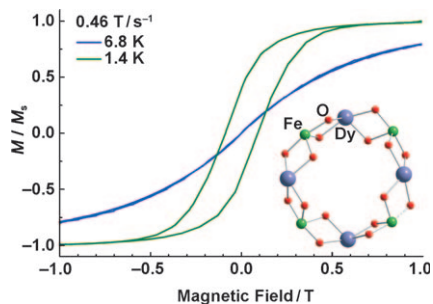
K. Betz, F. Streckenbach, A. Schnur,
T. Exner, W. Welte, K. Diederichs,
A. Marx* ————— 5181–5184



Structures of DNA Polymerases Caught
Processing Size-Augmented Nucleotide
Probes



The right fit: Synthetic nucleotide analogues are widely used to investigate the mechanisms that govern DNA polymerase selectivity—processes that are crucial for the survival of every living organism. The first crystal structures of size-augmented 4'-methylated and 4'-ethylated thymidine triphosphates (TTPs) in complex with a DNA polymerase have been elucidated (picture: superposition of three DNA polymerase structures in complex with TTPs).

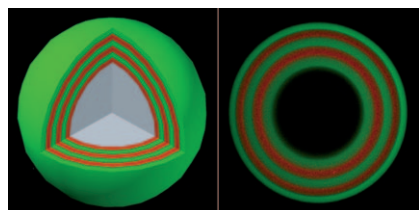


Ferromagnetic interactions in an Fe_4Dy_4 single-molecule magnet were studied using a combination of magnetic susceptibility measurements (see diagram; inset: cluster core) and ^{57}Fe Mössbauer spectroscopy.

Ferromagnetic Materials

D. Schray, G. Abbas, Y. Lan, V. Mereacre, A. Sundt, J. Dreiser, O. Waldmann, G. E. Kostakis, C. E. Anson, A. K. Powell* _____ **5185–5188**

Combined Magnetic Susceptibility Measurements and ^{57}Fe Mössbauer Spectroscopy on a Ferromagnetic $\{\text{Fe}^{\text{III}}_4\text{Dy}_4\}$ Ring



Encoding by encapsulation: A polymeric shell fabrication approach combines bio-molecule encapsulation with encoding. Striated polymeric shells, fabricated through an inwards diffusion of poly(al-lylamine) into the matrices of agarose microbeads, serves to encapsulate the biomolecules within the microcapsule. Encoding is performed through the color and/or thickness permutation of the striated polymeric shells (see picture).

Encoded Capsules

J. Bai, S. Beyer, W. C. Mak, R. Rajagopalan, D. Trau* _____ **5189–5193**

Inwards Buildup of Concentric Polymer Layers: A Method for Biomolecule Encapsulation and Microcapsule Encoding



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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Sister Journals _____ **5028–5030**

Keywords _____ **5194**

Authors _____ **5195**

Preview _____ **5197**

Corrigendum

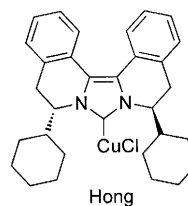
Copper-Free Asymmetric Allylic Alkylation with Grignard Reagents

In this Communication (DOI: 10.1002/anie.201000577), the ligand of Hong in Figure 1 was erroneously drawn. The correct structure is shown here.

O. Jackowski, A. Alexakis* — 3346–3350

Angew. Chem. Int. Ed. 2010, 49

DOI 10.1002/anie.201000577

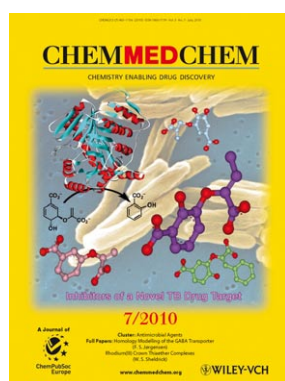


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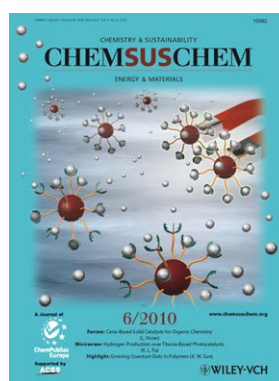
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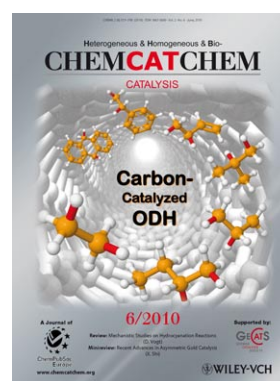
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