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. T. Scroggins, Y. Chi, J. M. J. Fréchet**
Polarity-Directed One-Pot Asymmetric Cascade Reactions Mediated by Two Catalysts in an Aqueous Buffer

*A. B. Chaplin, A. S. Weller**
B–H Activation at a Rhodium(I) Center: A Missing Link in the Transition-Metal-Catalyzed Dehydrocoupling of Amine–Boranes

M. Bandini, A. Eichholzer*
Enantioselective Gold-Catalyzed Allylic Alkylation of Indoles with Alcohols: Efficient Route to Functionalized Tetrahydrocarbazoles

*G. de Ruiter, E. Tartakovsky, N. Oded, M. E. van der Boom**
Sequential Logic Operations with Surface-Confined Polypyridyl Complexes Having Molecular Random Access Memory Features

*W. Li, P. H. C. Camargo, L. Au, Q. Zhang, M. Rycenga, Y. Xia**
Etching and Dimerization: A Simple and Versatile Route to Dimers of Silver Nanospheres with a Range of Sizes

*K. Fesko, M. Uhl, J. Steinreiber, K. Gruber, H. Griengl**
Biocatalytic Access to α,α-Dialkyl-α-Amino Acids by a Mechanism-Based Approach

*I. U. Khan, D. Zwanziger, I. Böhme, M. Javed, H. Naseer, S. W. Hyder, A. G. Beck-Sickinger**
Breast Cancer Diagnosis by Neuropeptide Y Analogues: From Synthesis to Clinical Application

*T. Yokoi, M. Yoshioka, H. Imai, T. Tatsumi**
Diversification of RTH-type Zeolite and its Catalytic Application

Y.-S. Li, F.-Y. Liang, H. Bux, A. Feldhoff, W.-S. Yang, J. Caro**
Metal–Organic Framework Molecular Sieve Membrane: Supported ZIF-7 Layer with High Hydrogen Selectivity by Microwave-Assisted Seeded Growth

S. Yamago, Y. Watanabe, T. Iwamoto*
Synthesis of [8]Cycloparaphenylene from a Square-Shaped Tetranuclear Platinum Complex $[\{Pt(cod)(4,4'\text{-biphenyl})\}_4]$

Author Profile

"The secret of being a successful scientist is a good mixture of imagination and hard work. My biggest inspiration is looking at art or doing nothing ..."
This and more about Jörg Rademann can be found on page 9218.

News

J. Cossy

C. Limberg

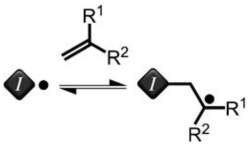
D. Sicker and S. Berger

Books

Highlights

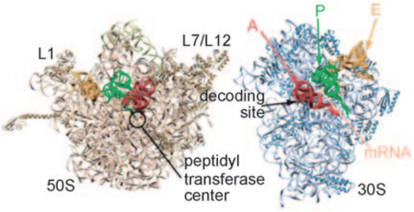
Radical Reactions

Reverse gear: Additions of primary radicals to sterically non-congested vinyl bonds may indeed not be as irreversible as commonly assumed. A ^{1}H-CIDNP NMR spectroscopic investigation on photoinitiated polymerization systems provides evidence that the addition of photolytically generated mesitoyl and phosphinoyl radicals to (meth)acrylate monomers at ambient temperatures may be reversible (see scheme; *I* = initiator).



Nobel Prize in Chemistry

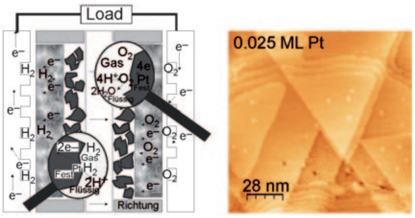
Lost in translation: Ribosomes have developed sophisticated mechanisms to ensure a precise translation of the genetic information into functional proteins. The Nobel Prize in Chemistry for 2009 goes to three researchers who provide us with valuable insights into the structure of ribosome using X-ray diffraction, thus improving our understanding of the translation process at the molecular level.



Essays

Energy Generation and Storage

Carnot versus electrochemistry: This essay critically compares the advantages and disadvantages of Carnot-cycle-based and electrochemical methods for the generation and storage of energy (see picture; left: PEM fuel cell; right: Au(111) model surface covered with 0.025 monolayers of Pt). The views of Wilhelm Ostwald (1853–1932) and today's understanding of energy conversion are contrasted.



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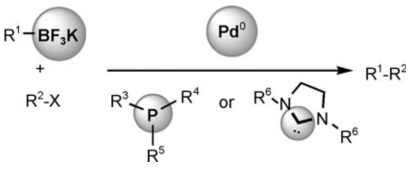
Reviews

Palladium Catalysis

G. A. Molander,* B. Canturk 9240 – 9261

Organotrifluoroborates and Monocoordinated Palladium Complexes as Catalysts—A Perfect Combination for Suzuki–Miyaura Coupling



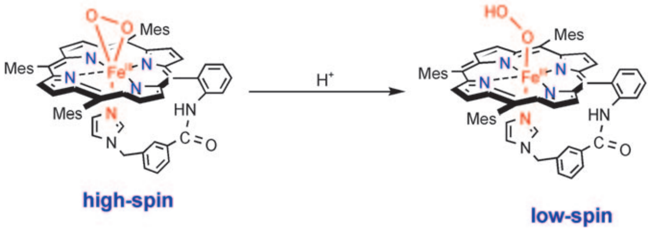
Hitting the sweet spot: The combination of organotrifluoroborates and monocoordinated palladium complexes as catalysts in the Suzuki–Miyaura coupling reaction provides a powerful method for the creation of carbon–carbon bonds. The advantages of organotrifluoroborates include the numerous functional groups that are tolerated in the substrate, the mild reaction conditions, and the possibility to use different types of reagents.

Communications

Enzyme Models

J.-G. Liu, T. Ohta, S. Yamaguchi, T. Ogura, S. Sakamoto, Y. Maeda, Y. Naruta* 9262 – 9267

Spectroscopic Characterization of a Hydroperoxo–Heme Intermediate: Conversion of a Side-On Peroxo to an End-On Hydroperoxo Complex

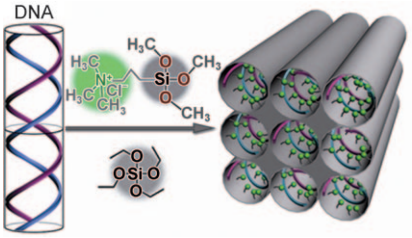


Modeling job: Protonation of a closed seven-coordinate side-on heme peroxide can switch its spin state from high- to low-spin and convert the η^2 binding fashion into a monodentate configuration to afford the corresponding hydroperoxide (see scheme). The end-on low-spin ferric hydroperoxo–heme species bear a covalently appended axial imidazole ligand and are easily prepared.

Silica Mineralization

C. Jin, L. Han, S. Che* 9268 – 9272

Synthesis of a DNA–Silica Complex with Rare Two-Dimensional Square *p4mm* Symmetry



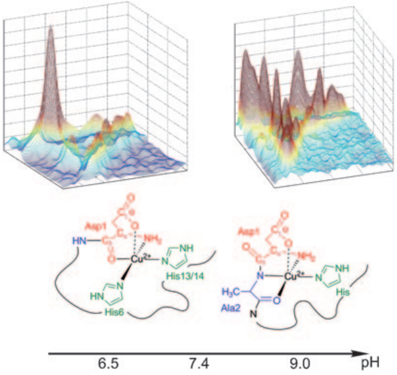
Zipped together: The title system was synthesized by using a quaternary ammonium silane as a DNA-condensing agent and a co-condenser with the silica source. The small interaxial separation in electrostatic DNA–DNA "zippers" and silica walls formed between diagonally positioned DNA strands are optimal for formation of the *p4mm* structure.

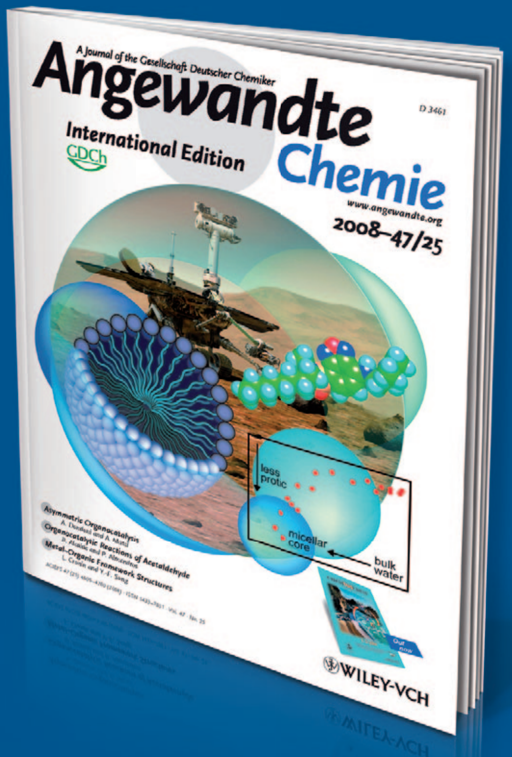
Peptide Interactions

P. Dorlet,* S. Gambarelli, P. Faller, C. Hureau 9273 – 9276

Pulse EPR Spectroscopy Reveals the Coordination Sphere of Copper(II) Ions in the 1–16 Amyloid-β Peptide: A Key Role of the First Two N-Terminus Residues

Ligand sphere revealed: Cu ions were proposed to be linked to the aggregation of the amyloid-β peptide in Alzheimer's disease. However, unambiguous identification of the Cu ligands has remained difficult. The use of various EPR spectroscopies with specific isotopic labeling now allowed the assignment of the Cu^{II} ligands for both complexes present at physiological pH value (see 3D plots and structures). The results indicate that the peptide's first two amino acids are important for coordination and probably aggregation.

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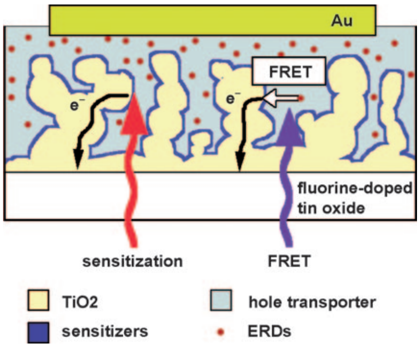
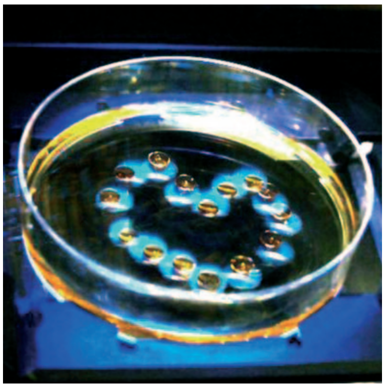
Running relay: Incorporating an energy-relay dye (ERD) into the hole transporter of a dye-sensitized solar cell increased power-conversion efficiency by 29% by extending light harvesting into the blue region. In the operating mechanism (see picture), absorption of red photons by the sensitizer transfers an electron into TiO_2 and a hole into the electrolyte. Blue photons absorbed by the ERD are transferred by FRET to the sensitizer.



Molecular Solar Cells

J.-H. Yum, B. E. Hardin, S.-J. Moon,
E. Baranoff, F. Nüesch, M. D. McGehee,
M. Grätzel,*
M. K. Nazeeruddin* ——— 9277–9280

Panchromatic Response in Solid-State Dye-Sensitized Solar Cells Containing Phosphorescent Energy Relay Dyes

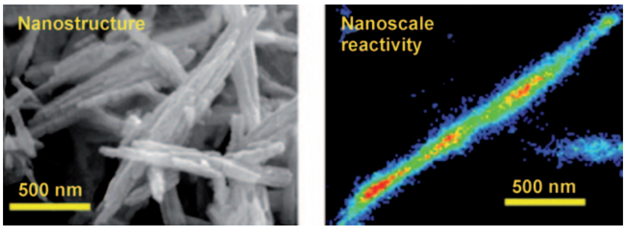


Ace of hearts: Liquid droplets can be manipulated in a controlled fashion along trajectories of any desired shape (such as a heart, see picture) by using light to create a wavelength-dependent interfacial tension gradient at a liquid/liquid interface. In this new phenomenon, the “chromocapillary effect”, an interfacial flow generates droplet motion in the direction opposite to the gradient.

Photocontrolled Motion

A. Diguet, R.-M. Guillermic, N. Magome,
A. Saint-Jalmes, Y. Chen, K. Yoshikawa,
D. Baigl* ——— 9281–9284

Photomanipulation of a Droplet by the Chromocapillary Effect



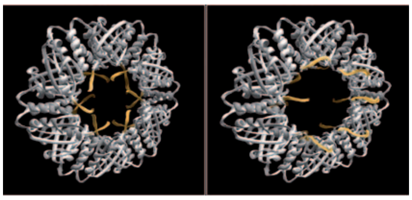
Its a small world: Nanoscale reactivity maps of working heterogeneous catalysts are recorded under in situ conditions by localizing single fluorescent reaction products (see picture). This approach allows quantification of the reactivity of catalytic nanodomains.

Heterogeneous Catalysis

M. B. J. Roeffaers, G. De Cremer,
J. Libeert, R. Ameloot, P. Dedecker,
A.-J. Bons, M. Bückins, J. A. Martens,
B. F. Sels, D. E. De Vos,
J. Hofkens* ——— 9285–9289

Super-Resolution Reactivity Mapping of Nanostructured Catalyst Particles

Ringing the changes: A selective, controlled, and tunable attachment of proteins to a metal or to insulating surfaces is presented. A ring-shaped protein encapsulating SiO_2-binding peptides (see picture: yellow) was engineered to expose multiple binding sites simply by changing solvent conditions, thereby creating a single monolayer without the need for surface modification.



Protein Engineering

A. Heyman, I. Medalsy, O. Bet Or,
O. Dgany, M. Gottlieb, D. Porath,*
O. Shoseyov* ——— 9290–9294

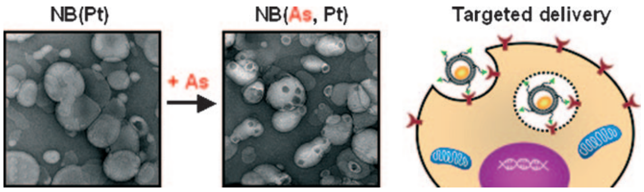
Protein Scaffold Engineering Towards Tunable Surface Attachment

Contents

Nanomedicine

H. Chen, S. Pazicni, N. L. Krett, R. W. Ahn,
J. E. Penner-Hahn, S. T. Rosen,
T. V. O'Halloran* ________ **9295 – 9299**

Coencapsulation of Arsenic- and Platinum-based Drugs for Targeted Cancer Treatment

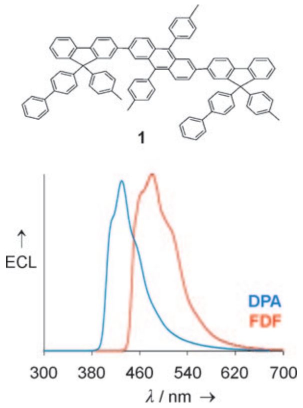


Two in one: A novel strategy for efficiently coencapsulating both arsenic- and platinum-based drugs into 100 nm-scale liposomes (NBs) relies on the formation of $\mathrm{Pt^{II}}$–$\mathrm{As^{III}}$ adducts. This co-loaded system presents a robust platform for further modification with targeting ligands and affords a method of improving the therapeutic efficacy of anticancer agents.

Optical Materials

K. M. Omer, S.-Y. Ku, K.-T. Wong,*
A. J. Bard* ________ **9300 – 9303**

Efficient and Stable Blue Electrogenerated Chemiluminescence of Fluorene-Substituted Aromatic Hydrocarbons

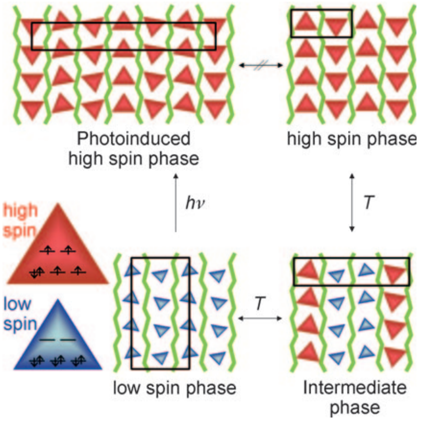


Properly shielded: The fluorene groups used as capping agents for new diphenylanthracene (DPA), pyrene, and anthracene derivatives impart steric hindrance which prevents interchromophore interactions, giving these molecules high photoluminescence quantum yields. Fluorene-based DPA (**1**) is characterized by a highly efficient and stable blue electrogenerated chemiluminescence (ECL).

Spin Crossover

N. Bréfuel , H. Watanabe, L. Toupet,
J. Come, N. Matsumoto, E. Collet,*
K. Tanaka, J.-P. Tuchagues* **9304 – 9307**

Concerted Spin Crossover and Symmetry Breaking Yield Three Thermally and One Light-Induced Crystallographic Phases of a Molecular Material

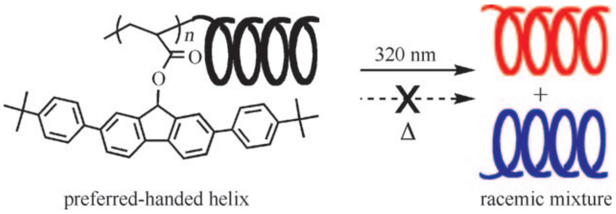


Four crystal phases are accessible by thermally and light-induced spin crossover associated with symmetry breaking for $[\mathrm{Fe^{II}H_2L^{2Me}H_2L^{2Me}}](\mathrm{PF_6})_2$ ($\mathrm{H_2L^{2Me}}$ is an acyclic hexadentate $\mathrm{N_6}$ Schiff base). In this novel molecular material, the arrays of $\mathrm{Fe^{II}}$ complex cations (high-spin: red triangles; low-spin: blue triangles) are separated by layers of counteranions (green zigzag lines).

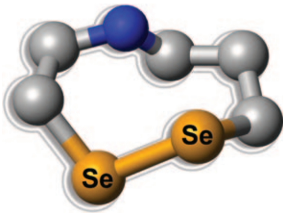
Photoinduced Stereomutation

T. Sakamoto, Y. Fukuda, S.-i. Sato,
T. Nakano* ________ **9308 – 9311**

Photoinduced Racemization of an Optically Active Helical Polymer Formed by the Asymmetric Polymerization of 2,7-Bis(4-*tert*-butylphenyl)fluoren-9-yl Acrylate



A trick of light: An optically active preferred-handed helical polymer synthesized by asymmetric anionic polymerization underwent stereomutation upon photoirradiation, whereas the helix remained stable upon heating (see picture). This photoinduced racemization of a synthetic helical polymer occurred without any changes in chemical bonding, such as bond formation, bond cleavage, or the isomerization of a double bond.

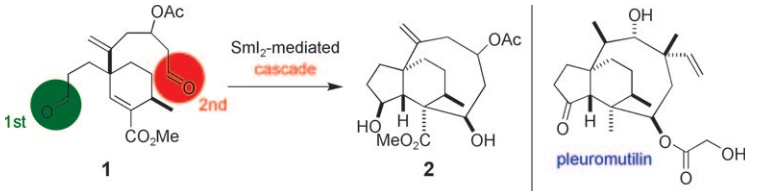


Se-ing is believing: Many proteins are cross-braced by disulfide bonds that frequently play key roles in protein structure, folding, and function. Unfortunately, the methods available for assignment of disulfide-bond connectivities in proteins are technically difficult and prone to misinterpretation. Now disulfide bond connectivities in native proteins can be visualized directly using ^{77}Se NMR spectroscopy.

Protein Structures

M. Mobli, A. D. de Araújo, L. K. Lambert,
G. K. Pierens, M. J. Windley,
G. M. Nicholson, P. F. Alewood,
G. F. King* ——— **9312 – 9314**

Direct Visualization of Disulfide Bonds through Diselenide Proxies Using ^{77}Se NMR Spectroscopy

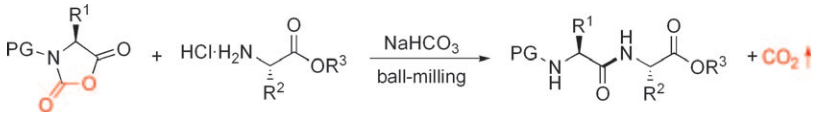


Waiting in line: Aldehyde groups take turns reacting in a SmI_2-mediated cyclization cascade to form the skeleton **2** of the antibacterial natural product pleuromutilin. Two rings and four contiguous stereocenters are constructed during the cascade with complete diastereocontrol.

Natural Product Synthesis

M. D. Helm, M. Da Silva, D. Sucunza,
T. J. K. Findley, D. J. Procter* **9315 – 9317**

A Dialdehyde Cyclization Cascade: An Approach to Pleuromutilin

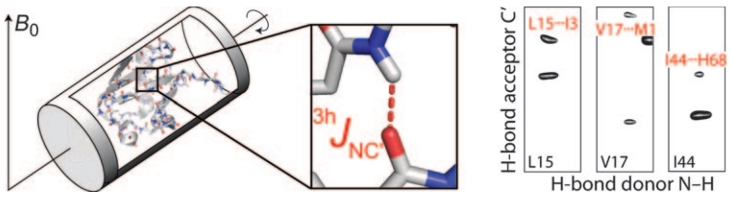


A crush on sweetness! The coupling of a urethane-protected *N*-carboxyanhydride of an amino acid with another amino acid derivative under ball-milling conditions gives a protected dipeptide in very high yield (see scheme; PG: protecting group). The reaction takes place in the solid state. The synthesis was applied to the preparation of a tripeptide and the sweetener aspartame, without any organic solvent or purification.

Synthetic Methods

V. Declerck, P. Nun, J. Martinez,
F. Lamaty* ——— **9318 – 9321**

Solvent-Free Synthesis of Peptides



Hydrogen bonds are ubiquitous interactions in proteins, and are important for their folding and functionality. Scalar coupling constants across hydrogen bonds in the protein backbone, some as small as 0.5 Hz, can be directly measured in the solid state by NMR spectroscopy (see figure). The nuclei on both sides of the hydrogen bond can be identified and the size of the coupling constant can be measured accurately.

NMR Spectroscopy

P. Schanda,* M. Huber, R. Verel, M. Ernst,
B. H. Meier* ——— **9322 – 9325**

Direct Detection of $^{3h}J_{NC'}$ Hydrogen-Bond Scalar Couplings in Proteins by Solid-State NMR Spectroscopy

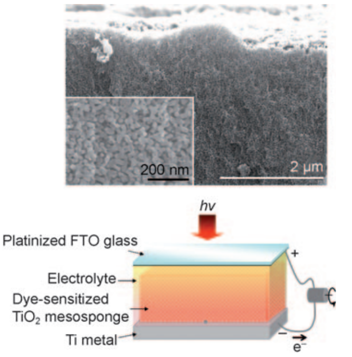
Contents

Mesoporous Layers

D. Kim, K. Lee, P. Roy, B. I. Birajdar, E. Spiecker, P. Schmuki* —— **9326 – 9329**

Formation of a Non-Thickness-Limited Titanium Dioxide Mesosponge and its Use in Dye-Sensitized Solar Cells

Etch a sketch: Robust TiO_2 mesoporous layers can be fabricated on Ti surfaces by a combination of non-thickness-limited anodization and selective etching. Layers more than 50 μm thick with highly regular feature and pore sizes in the range 5–10 nm can be produced (see picture, FTO = fluorine doped tin oxide). The layers are highly flexible, well-adhered, and can be used directly after appropriate annealing in efficient dye-sensitized solar cells.

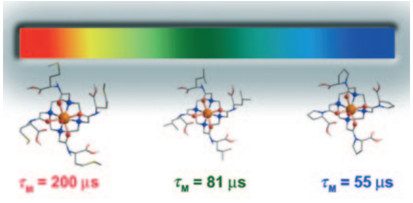


Imaging Techniques

S. Viswanathan, S. J. Ratnakar, K. N. Green, Z. Kovacs, L. M. De León-Rodríguez, A. D. Sherry* —— **9330 – 9333**

Multi-Frequency PARACEST Agents Based on Europium(III)-DOTA-Tetraamide Ligands

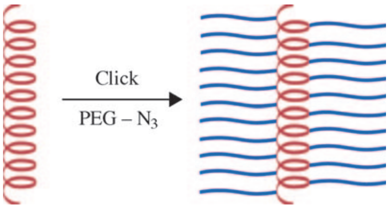
Colorful palette: A new class of highly selective Eu^{3+}-based multi-frequency PARACEST agents is reported. The complexes can be tuned when administered simultaneously thereby allowing for the possibility of monitoring multiple biomarkers in parallel. PARACEST = paramagnetic chemical exchange saturation transfer.



Polymer Brushes

A. C. Engler, H.-i. Lee, P. T. Hammond* —— **9334 – 9338**

Highly Efficient “Grafting onto” a Polypeptide Backbone Using Click Chemistry

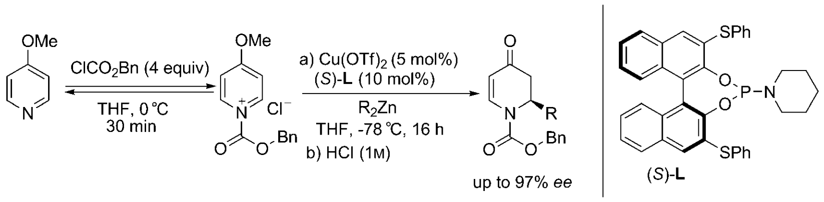


“Clicked” into place: Densely grafted poly(γ-propargyl-L-glutamate)-g-poly(ethylene glycol) polypeptides have been synthesized by combining ring-opening polymerization of *N*-carboxyanhydrides with click chemistry. Various lengths of poly(ethylene glycol) (PEG) side chains (750 g mol^{-1} to 5000 g mol^{-1}) were attached to a rigid α-helical poly(γ-propargyl-L-glutamate); extremely high grafting efficiencies of over 96% were achieved.

Asymmetric Catalysis

M. Á. Fernández-Ibáñez, B. Maciá, M. G. Pizzuti, A. J. Minnaard,* B. L. Feringa* —— **9339 – 9341**

Catalytic Enantioselective Addition of Dialkylzinc Reagents to *N*-Acylpyridinium Salts

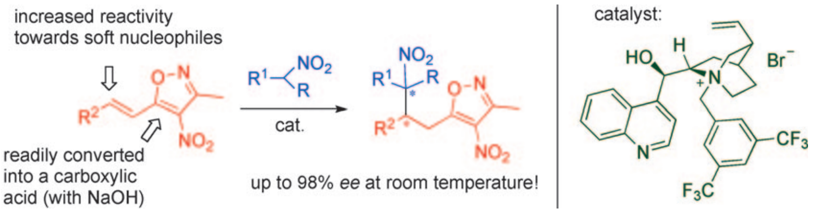


A pinch of salt: The first catalytic addition of dialkylzinc reagents to *N*-acylpyridinium salts with good yields and excellent enantioselectivities uses a copper–(*S*)-**L** complex as the catalyst. The versatility of the method is illustrated in the formal synthesis of the alkaloid (*R*)-coniine. Bn = benzyl, Tf = trifluoromethanesulfonyl.

Organocatalysis

A. Baschieri, L. Bernardi,* A. Ricci,
S. Suresh, M. F. A. Adamo* **9342 – 9345**

Catalytic Asymmetric Conjugate Addition of Nitroalkanes to 4-Nitro-5-styrylisoxazoles

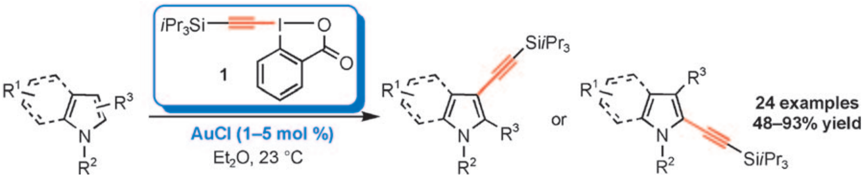


Nitro versus nitro: 4-Nitro-5-styrylisoxazoles were used as masked α,β-unsaturated carboxylic acids in the titled catalytic asymmetric transformation. The 4-nitroisoxazole core acts as an activator of the conjugated alkene and a latent carboxylate functionality. The reaction proceeded with 5 mol % of a readily prepared phase-transfer catalyst at room temperature with remarkable diastereo- and enantioselectivity (see scheme).

Direct Alkynylation

J. P. Brand, J. Charpentier,
J. Waser* **9346 – 9349**

Direct Alkynylation of Indole and Pyrrole Heterocycles

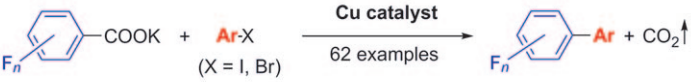


Easy does it: The unique properties of benziodoxolone alkynyl periodinane **1** and gold catalysts have allowed the development of a high yielding, operationally simple (room temperature, no dry solvents or inert conditions, commercially available catalyst) reaction for the introduction of silylacetylenes on a large range of indole and pyrrole heterocycles with a wide range of functional groups (see scheme).

C–C Coupling

R. Shang, Y. Fu, Y. Wang, Q. Xu, H.-Z. Yu,
L. Liu* **9350 – 9354**

Copper-Catalyzed Decarboxylative Cross-Coupling of Potassium Polyfluorobenzoates with Aryl Iodides and Bromides



For copper only: The decarboxylative cross-coupling of readily accessible and nonvolatile potassium polyfluorobenzoates with aryl iodides and bromides using a copper catalyst provides polyfluorobiaryls and polyfluorostilbenes in excellent yields (see scheme). Mechanistic analyses are reported for the title reaction.

Chemoenzymatic Synthesis

K. Baer, M. Kraußer, E. Burda,
W. Hummel, A. Berkessel,
H. Gröger* **9355 – 9358**

Sequential and Modular Synthesis of Chiral 1,3-Diols with Two Stereogenic Centers: Access to All Four Stereoisomers by Combination of Organo- and Biocatalysis

Biocompatible: A modular chemoenzymatic synthesis (see scheme) based on asymmetric organo- and biocatalytic reaction sequences allows the sequential construction of both stereogenic centers of 1,3-diols and leads to all four possible stereoisomers in enantiomerically pure form. The biocompatibility of the organocatalytic aldol reaction allows its direct use in the subsequent enzymatic reduction without the need for a work-up step.

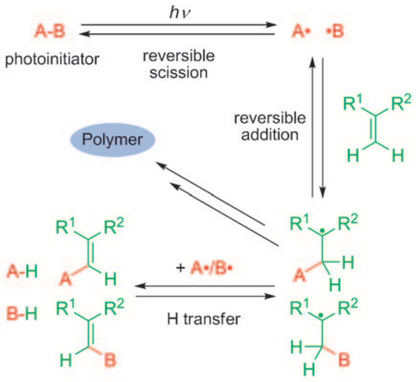
Contents

Radical Polymerization

M. Griesser, D. Neshchadin, K. Dietliker, N. Moszner, R. Liska, G. Gescheidt* ______ **9359 – 9361**

Decisive Reaction Steps at Initial Stages of Photoinitiated Radical Polymerizations

The first addition of photoinitiator radicals formed by the photolysis of a bisacylphosphine oxide photoinitiator to an acrylate double bond proceeds reversibly (see scheme; R^1 = tBu, H; R^2 = MeOC(=O), BuOC(=O)). Moreover, hydrogen transfer between substituted benzoyl radicals and the growing radical chain explains the formation of aldehydes in such a transformation.

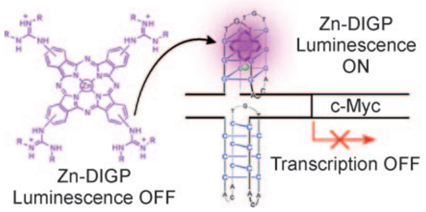


G-Quadruplex DNA

J. Alzeer, B. R. Vummidi, P. J. C. Roth, N. W. Luedtke* ______ **9362 – 9365**

Guanidinium-Modified Phthalocyanines as High-Affinity G-Quadruplex Fluorescent Probes and Transcriptional Regulators

Fluorescence is ON and transcriptional control is OFF when the guanidinium-modified zinc phthalocyanine Zn-DIGP binds a G-quadruplex DNA from the c-Myc promoter. With an equilibrium dissociation constant K_d of less than 2 nM, this interaction is the strongest binding interaction between a G-quadruplex structure and a small molecule reported to date.

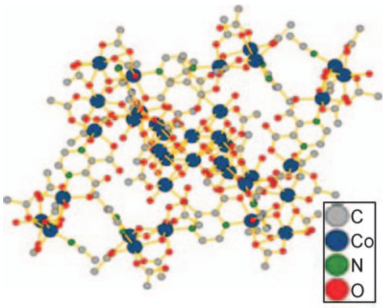


Metal Clusters

P. Alborés,* E. Rentschler* _ **9366 – 9370**

A Co$_{36}$ Cluster Assembled from the Reaction of Cobalt Pivalate with 2,3-Dicarboxypyrazine

A record Co$_{36}$ cluster is prepared. This mixed-valent compound containing Co^{II} and Co^{III} centers is formed in the reaction of a dinuclear cobalt pivalate species with the polydentate 2,3-dicarboxypyrazine ligand. In terms of magnetic properties it behaves as a {Co$_{16}$–Co$_{16}$} supramolecular dimer in which the $S = 4$ spin ground states of each monomer do not interact.



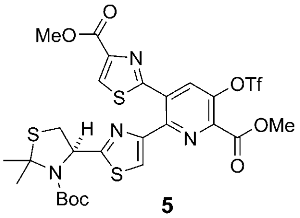
Supporting information is available on www.angewandte.org (see article for access details).

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

Service

Corrigendum

The correct structural formula of compound **5** in Scheme 1 of this Communication appears below. The authors apologize for this oversight.



5

Aza-Wittig-Supported Synthesis of the A Ring of Nosiheptide

J.-Y. Lu, M. Riedrich, M. Mikyna, H.-D. Arndt* **8137–8140**

Angew. Chem. Int. Ed. **2009**, *48*

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Corrigendum

In this Communication, the discussion of work by the Kraus research group was not precisely expressed and should be corrected to the following: Kraus and Wei[3d] reported that **7** and its diastereomer, which were claimed to be isolated as by-products in their elegant synthesis of racemic hyperolactone C, could not be converted into a lactone using heat, acid (PTSA), or base (*t*BuOK, NaH, or KH) catalysis. However, careful analysis and comparison of the NMR data of **13** (1:1 mixture of diastereomers) with both the by-products reported by Kraus and Wei indicated that they were identical (see the Supporting Information).

Moreover, the value of $\delta = 155.9$ ppm in the ^{13}C NMR data listed for compound **13** in the Supporting Information should be removed. The authors are grateful to Prof. David Hodgson of Oxford University for pointing this out.

Construction of Two Vicinal Quaternary Carbons by Asymmetric Allylic Alkylation: Total Synthesis of Hyperolactone C and (−)-Biyouyanagin A

C. Du, L. Li, Y. Li, Z. X. Xie* **7853–7856**

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