



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:

Y. Fu, Q. Dai, W. Zhang, J. Ren, T. Pan,* C. He*

The AlkB Domain of Mammalian ABH8 Catalyzes Hydroxylation of 5-Methoxycarbonylmethyluridine at the Wobble Position of tRNA

M. Willis, M. Götz, A. K. Kandalam, G. F. Ganteför,* P. Jena*

Hyperhalogens: A New Class of Highly Electronegative Species

V. Mazumder, M. Chi, K. L. More, S. Sun*

Synthesis and Characterization of Multimetallic Pd/Au and Pd/Au/FePt Core/Shell Nanoparticles

D. V. Esposito, S. T. Hunt, A. L. Stottlmyer, K. D. Dobson,

B. E. McCandless, R. W. Birkmire, J. G. Chen*

Low-Cost Hydrogen-Evolution Catalysts Based on Monolayer Platinum on Tungsten Monocarbide (WC) Substrates

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

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

R. Matsui, K. Seto, K. Fujita, T. Suzuki, A. Nakazaki, S. Kobayashi

Unusual E-Selective Ring-Closing Metathesis to Form Eight-Membered Rings

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

Building Hematite Nanostructures Using Oriented Attachment

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

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

Y. Zhang, G. M. Miyake, E. Y.-X. Chen*

Alane-Based Classical and Frustrated Lewis Pairs in Polymer Synthesis: Rapid Polymerization of Methyl Methacrylate and Naturally Renewable Methylene Butyrolactones to High-Molecular-Weight Polymers

Y. Matsuki, M. T. Eddy, R. G. Griffin, J. Herzfeld*

Rapid 3D MAS NMR Spectroscopy at Critical Sensitivity

S. Vellalath, I. Čorić, B. List*

N-Phosphinyl Phosphoramidate: A Chiral Brønsted Acid Motif for the Direct Asymmetric N,O-Acetalization of Aldehydes



K. Müller



R. Rinaldi

News

Prous Science Award:

K. Müller _____ 8560

Sofja Kovalevskaja Award:

R. Rinaldi _____ 8560



“My favorite subject at school was chemistry.

The most significant advance of the last 100 years has been rocket propulsion ...”

This and more about Thomas M. Klapötke can be found on page 8561.

Author Profile

Thomas M. Klapötke _____ 8561

Books

Profile der Zellbiologie

Lothar Jaenicke

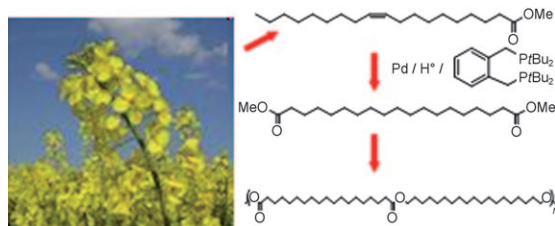
reviewed by U. Deichmann _____ 8562

Highlights

Plant-Based Plastics

D. J. Cole-Hamilton* — 8564–8566

Nature's Polyethylene



A new substitute for polyethylene is derived entirely from plant-based sources through methyl oleate or methyl erucate. Methoxycarbonylation with a palladium catalyst gives C_{19} or C_{24} α,ω -diesters,

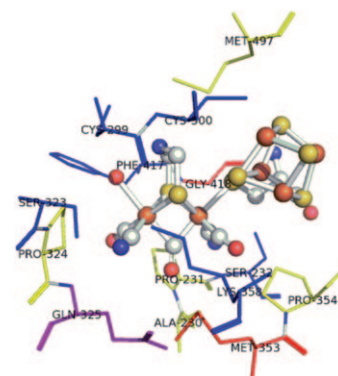
which are polymerized with their reduced alcohol forms to give polyesters with properties very like those of polyethylene (see scheme).

Hydrogenases

R. D. Bethel, M. L. Singleton,
M. Y. Darensbourg* — 8567–8569

The Modular Assembly of Clusters Is the Natural Synthetic Strategy for the Active Site of [FeFe] Hydrogenase

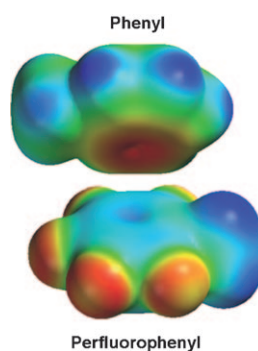
The 6Fe supercluster that comprises the [FeFe] hydrogenase active site has been shown to involve a modular buildup of iron–sulfur clusters. Only three accessory proteins are needed to produce the CN^- , CO, and $\mu-SCH_2NHCH_2S^-$ units that bind to the 2Fe2S subcluster precursor. The scaffold/carrier protein inserts the pre-formed 2Fe subcluster into the apoprotein through a channel, which then closes to encapsulate the completed active site.



Molecular Recognition

H. Robson Marsden, J. G. E. M. Fraaije,
A. Kros* — 8570–8572

Introducing Quadrupole Interactions into the Peptide Design Toolkit

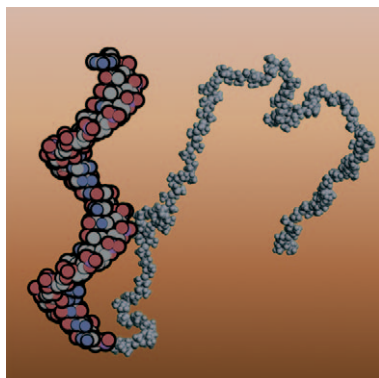


A star attraction: The electrostatic interactions between aromatic amino acid side chains having opposite quadrupole moments are sufficient to introduce specificity into peptide binding interactions. The demonstration of this principle expands the repertoire of chemical tools that can be used to engineer specific peptide–peptide interactions, thus paving the way to new functional assemblies.

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.



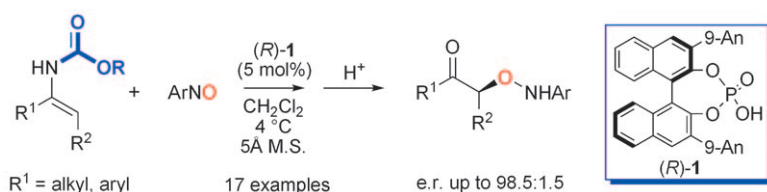
Skillful biohybrid: Combined biological and synthetic macromolecules make up an emerging structural class in material science. This Review describes the synthesis and potential applications of these compounds and DNA block copolymers in particular.

Reviews

DNA Block Copolymers

M. Kwak, A. Herrmann* — 8574–8587

Nucleic Acid/Organic Polymer Hybrid Materials: Synthesis, Superstructures, and Applications



A practically simple, highly enantioselective Brønsted acid catalyzed α -aminoxylation of enecarbamates extends the substrate scope for the α -aminoxylation to

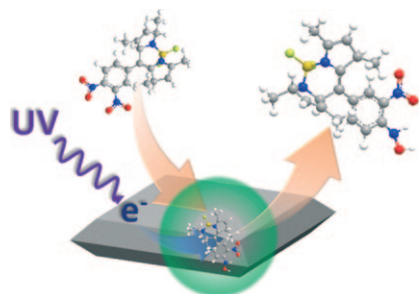
linear and aromatic ketones, allowing convergent and stereoselective access to valuable α -hydroxy ketones, β -amino alcohols, and *cis*-oxazolidinones.

Communications

Asymmetric Aminoxylation

M. Lu, Y. Lu, D. Zhu, X. Zeng, X. Li, G. Zhong* — 8588–8592

Chiral Brønsted Acid Catalyzed Enantioselective α -Aminoxylation of Enecarbamates

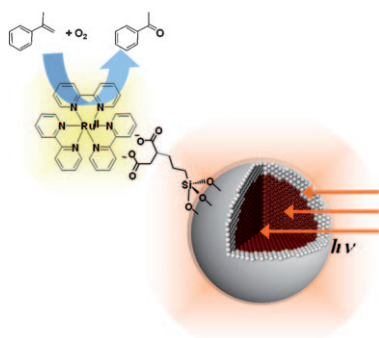


Single-molecule fluorescent probe: The formation of the highly fluorescent 4-NHOH form of a 3,4-dinitrophenyl-substituted boron dipyrromethane dye can be used to study interfacial electron transfer on individual TiO_2 particles (see picture; B yellow, C gray, F green, H white, O red). Kinetic and image analyses of the resulting fluorescence bursts reveal temporal dynamics of molecular interactions and reactive-site distributions.

Fluorescent Probes

T. Tachikawa,* N. Wang, S. Yamashita, S.-C. Cui, T. Majima* — 8593–8597

Design of a Highly Sensitive Fluorescent Probe for Interfacial Electron Transfer on a TiO_2 Surface



Plasmonic photocatalyst: Anchoring the dye $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine) on the surface of Ag nanoparticles coated with a thin SiO_2 layer (see picture) afforded a photocatalyst whose phosphorescence emission and photoinduced oxidation activity in the selective liquid-phase oxidation of styrene are efficiently enhanced through interaction with the localized surface plasmon resonance of the core Ag nanoparticles.

Photocatalysis

K. Mori, M. Kawashima, M. Che, H. Yamashita* — 8598–8601

Enhancement of the Photoinduced Oxidation Activity of a Ruthenium(II) Complex Anchored on Silica-Coated Silver Nanoparticles by Localized Surface Plasmon Resonance



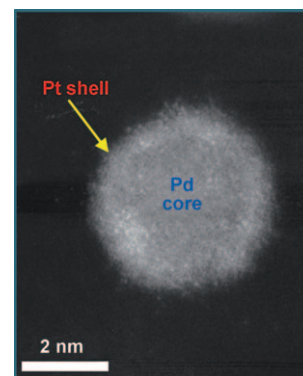
Core/Shell Nanoparticles

K. Sasaki, H. Naohara, Y. Cai, Y. M. Choi,
P. Liu, M. B. Vukmircovic, J. X. Wang,
R. R. Adzic* ————— **8602–8607**



Core-Protected Platinum Monolayer Shell
High-Stability Electrocatalysts for Fuel-
Cell Cathodes

More than skin deep: Platinum monolayers can act as shells for palladium nanoparticles to lead to electrocatalysts with high activities and an ultralow platinum content, but high platinum utilization. The stability derives from the core protecting the shell from dissolution. In fuel-cell tests, no loss of platinum was observed in 200 000 potential cycles, whereas loss of palladium was significant.

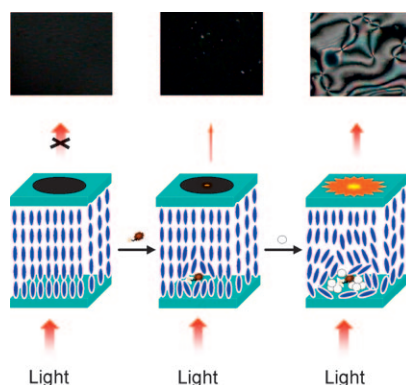


Liquid-Crystal Biosensors

H. Tan, S. Yang, G. Shen, R. Yu,
Z. Wu* ————— **8608–8611**



Signal-Enhanced Liquid-Crystal DNA
Biosensors Based on Enzymatic Metal
Deposition



No cloudiness with a silver lining: Deposition of metallic silver on a liquid-crystal substrate with attached DNA strands greatly alters the surface topology and induces a homeotropic-to-tiled transition of the LC molecules surrounding them, resulting in an obvious change in appearance from dark to birefringent (see picture; Ag: spheres). This enzymatic silver deposition is an excellent signal-enhancement strategy for LC optical amplification.

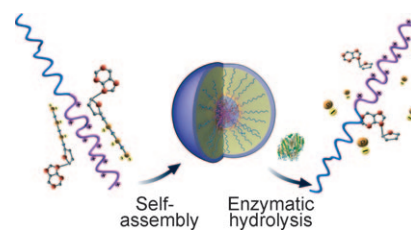
Superamphiphiles

C. Wang, Q. S. Chen, Z. Q. Wang,
X. Zhang* ————— **8612–8615**



An Enzyme-Responsive Polymeric
Superamphiphile

Responding to treatment: A superamphiphile is formed between a double-hydrophilic polymer (methoxy-poly(ethylene glycol)-*block*-poly(L-lysine hydrochloride)) and a natural enzyme-responsive molecule (adenosine 5'-triphosphate). The superamphiphile self-assembles into spherical aggregates, which, upon addition of enzymes, disassemble and release loaded molecules (see picture).



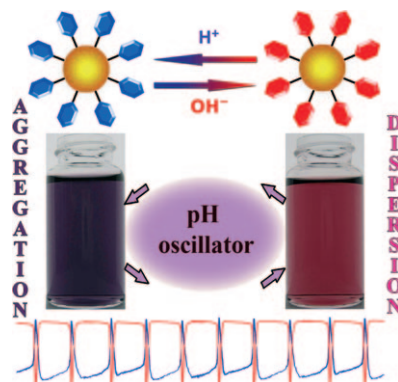
Nanoparticle Oscillators

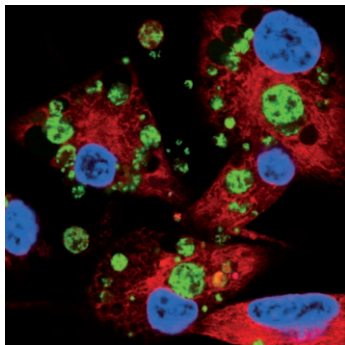
I. Lagzi, B. Kowalczyk, D. Wang,
B. A. Grzybowski* ————— **8616–8619**



Nanoparticle Oscillations and Fronts

Rhythmic nanoparticles: Chemical oscillations can be coupled to the dynamic self-assembly of nanoparticles. Periodic pH changes translate into protonation and deprotonation of the ligands that stabilize the nanoparticles, thus altering repulsive and attractive interparticle forces. In a continuous stirred-tank reactor, rhythmic aggregation and dispersion is observed; in spatially distributed media, propagation of particle aggregation fronts is seen.



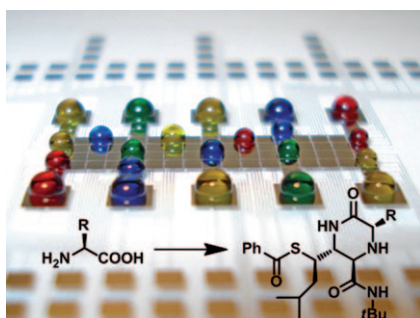


Pore medicine: Porous antigen-loaded degradable polyelectrolyte microspheres are produced in a straightforward way providing high encapsulation efficiencies and efficient internalization by antigen-presenting cells. This system could find application as multilayer capsules in gene and drug delivery and for enzymatic microreactors.

Drug Delivery

M. Dierendonck, S. De Koker, C. Cuvelier, J. Grooten, C. Vervaet, J.-P. Remon, B. G. De Geest* — 8620–8624

Facile Two-Step Synthesis of Porous Antigen-Loaded Degradable Polyelectrolyte Microspheres



Digital synthesis has been applied to the formation of peptide-based macrocycles and their analogues with side chains appended during late-stage aziridine ring-opening. Discrete nanoliter- to microliter-sized droplets of samples and reagents are controlled in parallel by applying a series of electrical potentials to an array of electrodes coated with a hydrophobic insulator.

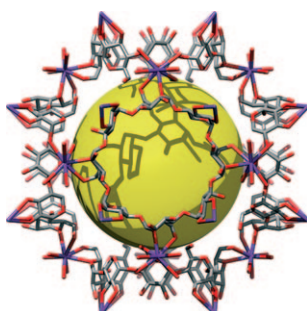
Microfluidic Synthesis

M. J. Jebrail, A. H. C. Ng, V. Rai, R. Hili, A. K. Yudin,* A. R. Wheeler* — 8625–8629

Synchronized Synthesis of Peptide-Based Macrocycles by Digital Microfluidics



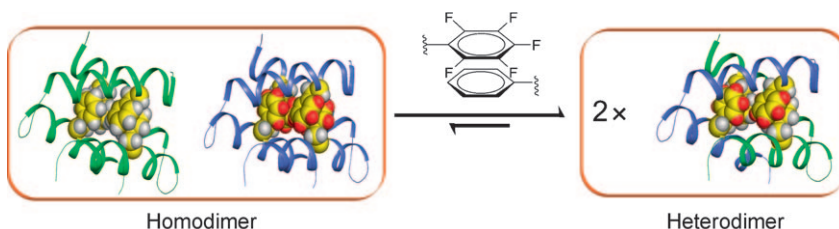
Let them eat MOFs: Take a spoonful of sugar (γ -cyclodextrin to be precise), a pinch of salt (most alkali metal salts will suffice), and a swig of alcohol (Everclear fits the bill), and you have a robust, nanoporous (Langmuir surface area $1320 \text{ m}^2 \text{ g}^{-1}$) metal–organic framework for breakfast (CD-MOF-1; see picture, C gray, O red, K purple; yellow sphere: pore).



Metal–Organic Frameworks

R. A. Smaldone, R. S. Forgan, H. Furukawa, J. J. Gassensmith, A. M. Z. Slawin, O. M. Yaghi, J. F. Stoddart* — 8630–8634

Metal–Organic Frameworks from Edible Natural Products



Quadrupole rules! The quadrupole stacking between aromatic and perfluoroaromatic rings is able to direct specific protein–protein interactions, resulting in

the exclusive formation of heterodimers upon mixing a pair of homodimers with aromatic and perfluoroaromatic cores.

Quadrupole Interactions

H. Zheng, J. Gao* — 8635–8639

Highly Specific Heterodimerization Mediated by Quadrupole Interactions

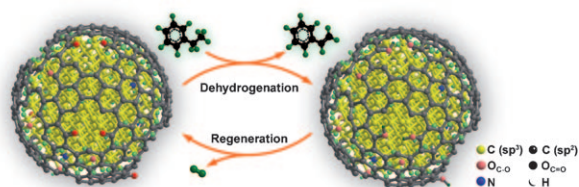


Nanodiamond Catalysts

J. Zhang, D. S. Su,* R. Blume, R. Schlögl,
R. Wang, X. G. Yang,
A. Gajović ————— 8640–8644



Surface Chemistry and Catalytic Reactivity
of a Nanodiamond in the Steam-Free
Dehydrogenation of Ethylbenzene



Hard core: A hybrid catalyst system for dehydrogenation of ethylbenzene comprises nanoparticles consisting of nanodiamond cores and highly curved, defective graphene shells (see picture). The

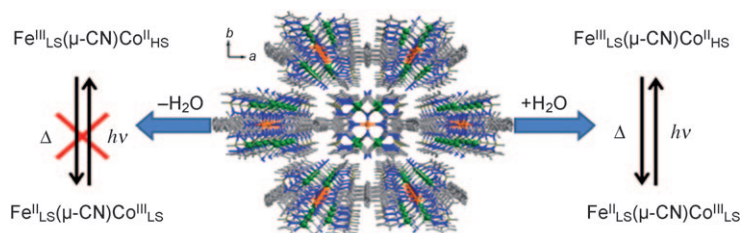
system exhibits high catalytic activity and selectivity over a long period of time. In contrast to industrial K-promoted Fe catalysts, steam decoking of the catalyst is not required.

Charge Transfer

T. Liu, Y.-J. Zhang, S. Kanegawa,
O. Sato* ————— 8645–8648



Water-Switching of Spin Transitions
Induced by Metal-to-Metal Charge
Transfer in a Microporous Framework



Water-switchable charge transfer: The microporous hydrated phase $\{[\text{Fe}(\text{Tp})(\text{CN})_3]_2\text{Co}(\text{bpe})\} \cdot 5 \text{H}_2\text{O}$ shows spin transition induced by metal-to-metal charge transfer (MMCT), but no MMCT is observed in the corresponding dehydrated

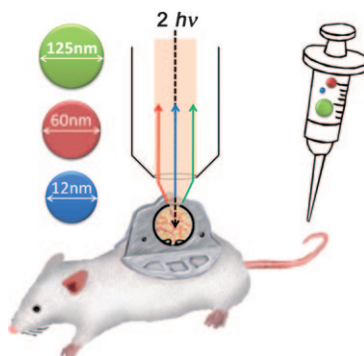
phase (see picture). Charge transfer can be reversibly switched through de- and rehydration. Tp = hydrotris(pyrazolyl)borate, bpe = 1,2-bis(4-pyridyl)ethane. Fe green, Co orange, N blue, O red, C gray, B dark yellow.

Medicinal Chemistry

Z. Popović, W. Liu, V. P. Chauhan, J. Lee,
C. Wong, A. B. Greytak, N. Insin,
D. G. Nocera, D. Fukumura, R. K. Jain,
M. G. Bawendi* ————— 8649–8652



A Nanoparticle Size Series for In Vivo
Fluorescence Imaging



A nanoparticle toolset was created within the size limits of 10–150 nm for probing size-dependent nanoparticle distribution in solid tumors. By using multiphoton intravital microscopy, the particles were tracked both spatially and temporally in the same tumor grown in a transparent window model.

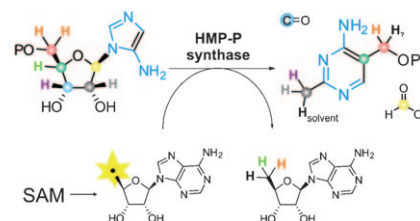
Thiamin Biosynthesis

A. Chatterjee, A. B. Hazra, S. Abdelwahed,
D. G. Hilmey, T. P. Begley* — 8653–8656

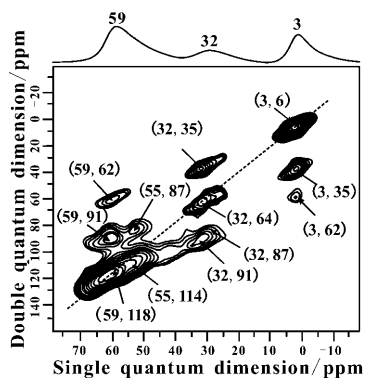


A “Radical Dance” in Thiamin
Biosynthesis: Mechanistic Analysis of the
Bacterial Hydroxymethylpyrimidine
Phosphate Synthase

Tricky things with ThiC: Hydroxymethylpyrimidine phosphate (HMP-P) synthase (ThiC) catalyzes one of the most complex rearrangement reactions in primary metabolism. Deuteration experiments show that under reducing conditions, in the presence of aminoimidazole ribonucleotide, the 5'-deoxyadenosyl radical generated at the active site of ThiC reacts directly with the substrate and performs two iterative hydrogen atom abstraction events to catalyze this rearrangement (see scheme; SAM = S-adenosylmethionine).



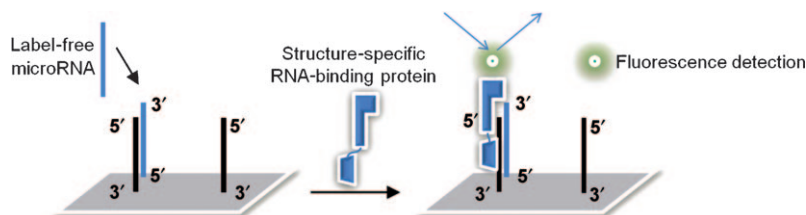
A zeolite dealumination mechanism is proposed on the basis of sensitivity-enhanced ^{27}Al DQ-MAS NMR spectra (see picture), which revealed for the first time the detailed evolution of extra-framework aluminum (EFAL) species and the spatial proximities of various aluminum species in dealuminated HY zeolites. Three types of EFAL species in close proximity to framework aluminum were identified.



Zeolites

Z. W. Yu, A. M. Zheng, Q. Wang, L. Chen,
J. Xu, J. P. Amoureux,*
F. Deng* 8657–8661

Insights into the Dealumination of Zeolite HY Revealed by Sensitivity-Enhanced ^{27}Al DQ-MAS NMR Spectroscopy at High Field



Biosensors

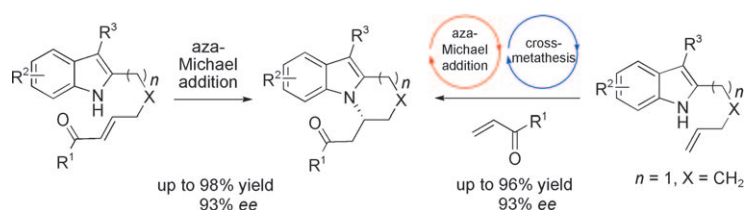
J. M. Lee, H. Cho, Y. Jung* 8662–8665

Fabrication of a Structure-Specific RNA Binder for Array Detection of Label-Free MicroRNA



Like an antibody: A novel structure-specific RNA-binding protein was designed to stably and specifically bind to surface-bound microRNAs. By acting like an antibody, this RNA binder enabled the

universal detection of hybridized micro-RNAs on array surfaces (see picture) without any enzymatic amplification or labeling reactions.



Asymmetric Catalysis

Q. Cai, C. Zheng, S.-L. You* 8666–8669

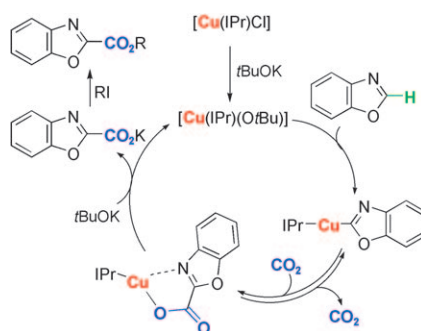
Enantioselective Intramolecular Aza-Michael Additions of Indoles Catalyzed by Chiral Phosphoric Acids



Two ways to win: The title reaction has been realized using chiral phosphoric acid catalysts to provide the heterocyclic products in excellent yields and with high

ee values. The polycyclic indoles were also constructed using an olefin cross-metathesis/intramolecular aza-Michael addition sequence.

Cooking with gas: Copper complexes serve as excellent catalysts for the direct carboxylation of aromatic heterocyclic C–H bonds with CO_2 , thereby offering an economical and environmentally benign process for the synthesis of heterocyclic carboxylic esters (see scheme; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). Some active intermediates of this reaction have been isolated and structurally characterized.



CO_2 Fixation

L. Zhang, J. Cheng, T. Ohishi,
Z. Hou* 8670–8673

Copper-Catalyzed Direct Carboxylation of C–H Bonds with Carbon Dioxide

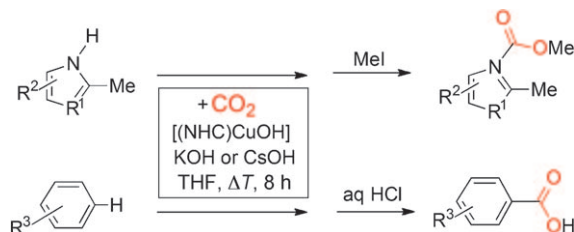


C–H/N–H Bond Functionalization

I. I. F. Boogaerts, G. C. Fortman,
M. R. L. Furst, C. S. J. Cazin,*
S. P. Nolan* ————— 8674–8677



Carboxylation of N–H/C–H Bonds Using
N-Heterocyclic Carbene Copper(I)
Complexes



Greenhouse gas makes good: A simple copper-mediated protocol has been developed where N–H or C–H bonds can be directly functionalized using an easily prepared catalyst. The novel [1,3-bis(2,6-

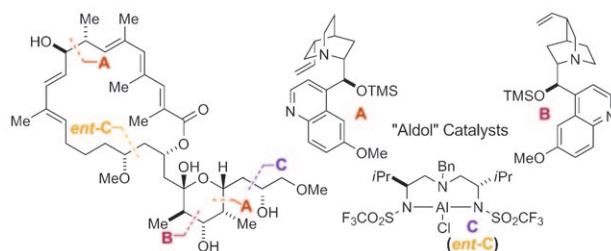
diisopropylphenyl)imidazol-2-ylidene]copper(I) hydroxide, [Cu(IPr)(OH)], permits the facile activation and carboxylation of N–H and C–H bonds with pK_a values of less than 27.7 (see scheme).

Catalytic Asymmetric Synthesis

T. R. Vargo, J. S. Hale,
S. G. Nelson* ————— 8678–8681



Catalytic Asymmetric Aldol Equivalents in
the Enantioselective Synthesis of the
Apoptolidin C Aglycone



Aldol replacement: Catalytic asymmetric ketene–aldehyde cycloadditions provide surrogates for traditional aldol additions in an enantioselective synthesis of apoptolidinone C, the aglycone of the potent

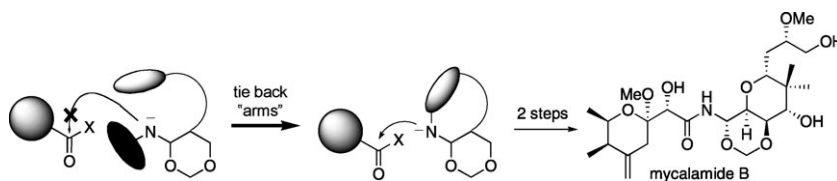
apoptosis regulator apoptolidin C. Eight of apoptolidinone C's ten stereocenters derive directly from these catalytic acetate or propionate aldol equivalents.

Natural Products Synthesis

J. C. Jewett, V. H. Rawal* — 8682–8685



Temporary Restraints To Overcome Steric
Obstacles: An Efficient Strategy for the
Synthesis of Mycalamide B



Restrain and release: A one-pot Mukaiyama–Michael/epoxidation sequence introduced three stereocenters, an intramolecular isocyanate trapping

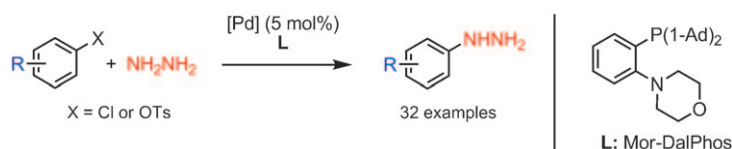
produced a rigid 10-membered cyclic carbamate, and the selective opening of the cyclic carbamate was used to reveal the fully constructed natural product.

Amination

R. J. Lundgren,
M. Stradiotto* ————— 8686–8690

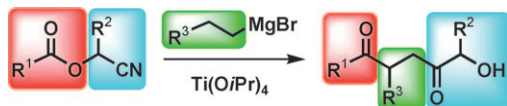


Palladium-Catalyzed Cross-Coupling of
Aryl Chlorides and Tosylates with
Hydrazine



Hydrazine is not a problem anymore: The title transformation is the first reaction to yield aryl hydrazines through the cross-coupling of aryl chlorides and tosylates with hydrazine. An appropriately designed

palladium catalyst allows this reaction to proceed rapidly under mild conditions, and with excellent chemoselectivity (see scheme; Ad = adamantyl, Ts = 4-toluene-sulfonyl).



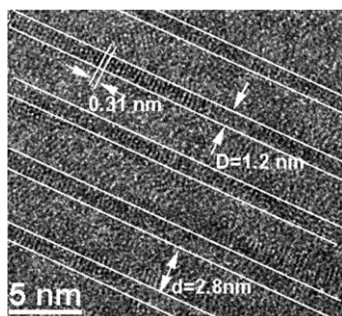
Double duty: In the presence of titanium isopropoxide, Grignard reagents were found to react with acyl cyanohydrins to give substituted 5-hydroxy-1,4-diketones

(see scheme). This new reaction involves a formal addition of a 1,2-dianion equivalent to both the ester and nitrile moieties.

Synthetic Methods

P. Setzer, A. Beauseigneur,
M. S. M. Pearson-Long,
P. Bertus* — 8691 – 8694

Titanium-Mediated Synthesis of
1,4-Diketones from Grignard Reagents
and Acyl Cyanohydrins

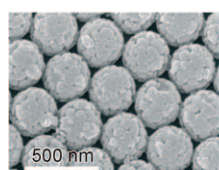


Down to the thin wire: A facile colloidal chemistry method is demonstrated for the controlled growth of highly uniform ultrathin single-crystal ZnS nanowires with a magic-size diameter as low as 1.2 nm (see HRTEM image). These ultrathin nanowires could find broad use in sensors, photodetectors, and host materials for diluted magnetic semiconductors.

Nanowires

Z. Deng, H. Yan, Y. Liu* — 8695 – 8698

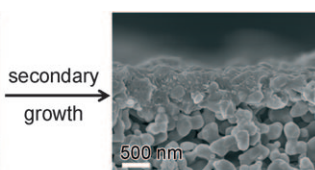
Controlled Colloidal Growth of Ultrathin
Single-Crystal ZnS Nanowires with a
Magic-Size Diameter



polycrystalline aggregates



porous α -alumina support



Zeolite Membranes

W. C. Yoo, J. A. Stoeger, P.-S. Lee,
M. Tsapatsis, A. Stein* — 8699 – 8703

High-Performance Randomly Oriented
Zeolite Membranes Using Brittle Seeds
and Rapid Thermal Processing



MFI zeolite membranes with high flux and high separation factors for xylene isomer separation were fabricated by combining several unique processing steps. These include 1) use of brittle seeds prepared by confined synthesis, 2) rubbing and leveling methods to obtain randomly oriented

seed layers, 3) secondary hydrothermal growth to produce thin zeolite films, and 4) rapid thermal processing to remove structure-directing agents while minimizing crack formation (see picture; scale bar 500 nm).



A cyclic phosphagermacarbene is formed by a [3+2] cycloaddition between the 1,3-dipolar $\text{Ge}=\text{C}=\text{P}$ unit of a phosphagermaallene and an acetylene (see scheme; Tip = 2,4,6- $i\text{Pr}_3\text{C}_6\text{H}_3$). The car-

bene undergoes C–H insertion or is trapped by a second equivalent of acetylene derivative, and its existence and reactivity was supported by DFT calculations.

Heterocyclic Carbenes

D. Ghereg, E. André, J.-M. Sotiropoulos,
K. Miqueu, H. Gornitzka,*
J. Escudié* — 8704 – 8707

1,3-Dipole Behavior of Phosphagerma-
allene $\text{Tip}(\text{tBu})\text{Ge}=\text{C}=\text{P}\text{Mes}^*$ Leading to a
Phosphagermaheterocyclic Carbene

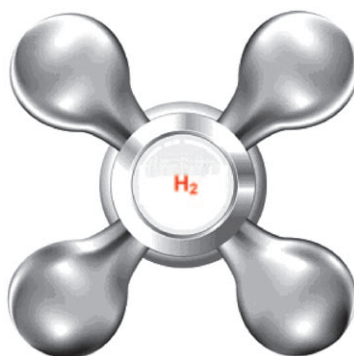


Hydrogen Storage

T. W. Graham, C.-W. Tsang, X. Chen,
R. Guo, W. Jia, S.-M. Lu, C. Sui-Seng,
C. B. Ewart, A. Lough, D. Amoroso,*
K. Abdur-Rashid* — 8708–8711



Catalytic Solvolysis of Ammonia Borane



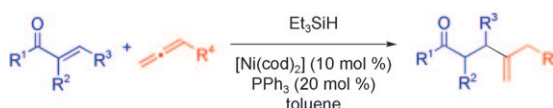
Hydrogen on tap: A homogeneous catalyst system for the rapid and quantitative solvolysis of ammonia borane (AB) has been developed. The iridium catalyst is remarkably stable and can be reused with no observable degradation in activity. In the absence of solvent, the mixture of catalyst and AB efficiently generates hydrogen upon exposure to water vapor, thereby resulting in a system with considerable hydrogen storage capacity (see picture).

Synthetic Methods

W. Li, N. Chen,
J. Montgomery* — 8712–8716



Regioselective Nickel-Catalyzed Reductive Couplings of Enones and Allenes



Alkenes made easy: In a complement to coupling processes of terminal alkynes, the reductive coupling of enones and allenes provides access to conjugate addition products that possess a 1,1-

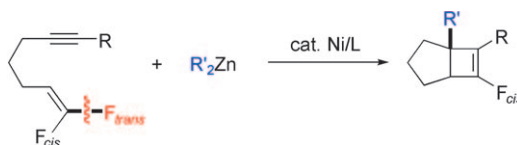
disubstituted alkene (see scheme; cod = 1,5-cyclooctadiene). The solvent composition and reducing agent must be carefully matched to allow high levels of regioselectivity to be observed.

C–F Activation

M. Takachi, Y. Kita, M. Tobisu,
Y. Fukumoto, N. Chatani* — 8717–8720



Nickel-Catalyzed Cyclization of Difluoro-Substituted 1,6-Enynes with Organozinc Reagents through the Stereoselective Activation of C–F Bonds: Synthesis of Bicyclo[3.2.0]heptene Derivatives



Quite a gem: A nickel-catalyzed cyclization of 1,6-enynes, bearing a gem-difluoro group at the olefinic terminus, with organozinc reagents gives the title compounds (see scheme). One of the fluorine atoms

is stereoselectively replaced by the R' group of R'2Zn, indicating the involvement of the stereoselective activation of a C–F bond.

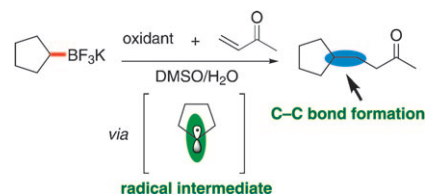
Radical Reactions

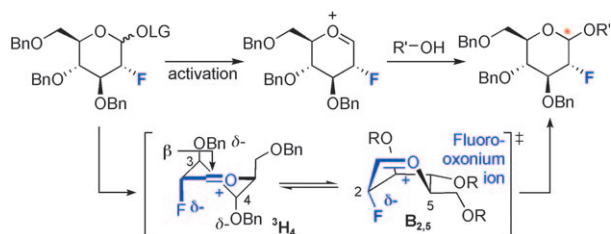
G. Sorin, R. Martinez Mallorquin,
Y. Contie, A. Baralle, M. Malacria,
J.-P. Goddard,
L. Fensterbank* — 8721–8723



Oxidation of Alkyl Trifluoroborates: An Opportunity for Tin-Free Radical Chemistry

Organotrifluoroborates have been oxidized by copper(II) salts and Dess–Martin periodinane via radical intermediates, as evidenced by TEMPO spin-trapping experiments. This new method of radical generation is compatible with functionalization and C–C bond formation through Giese-type addition reactions (see scheme; DMSO = dimethyl sulfoxide, TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy, free radical).





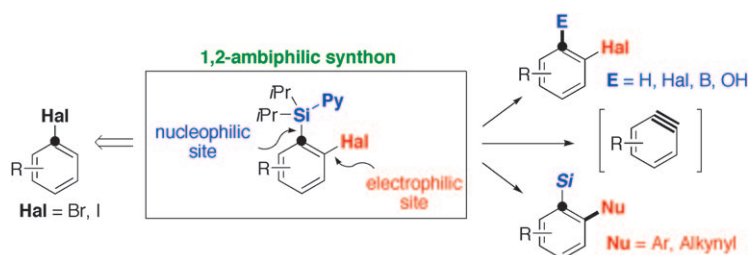
Everything's under control: A stabilizing fluorine electrostatic interaction has been exploited to control oxonium ion conformation in 2-fluoropyranose derivatives (see scheme). When matched with the inductive nature of the protecting groups,

the glycosyl donors were found to be highly selective (2- F^{Gluc} /benzyl $\rightarrow \beta$; 2- F^{Manno} /pivaloyl $\rightarrow \alpha$) leading to fluoro-glycostructures with excellent control over the anomeric configuration.

Fluoro Sugars

C. Bucher, R. Gilmour* — 8724–8728

Fluorine-Directed Glycosylation



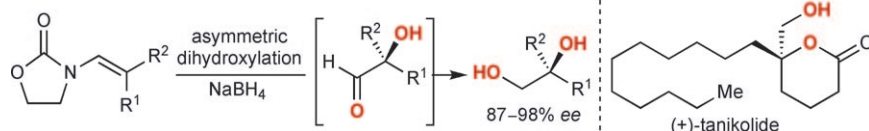
A general and efficient strategy to synthesize 1,2-ambiphilic aromatic and heteroaromatic synthons from haloarenes has been developed. The method involves installation of the PyDipSi directing group, and subsequent palladium-cata-

lyzed directed *ortho*-halogenation of aryl silanes (see scheme; Py = 2-pyridyl). The usefulness of these 1,2-ambiphilic building blocks was shown in their participation as both nucleophilic aryl silane and electrophilic aryl iodide moieties.

C–H Activation

A. S. Dudnik, N. Chernyak, C. Huang, V. Gevorgyan* — 8729–8732

A General Strategy Toward Aromatic 1,2-Ambiphilic Synthons: Palladium-Catalyzed *ortho*-Halogenation of PyDipSi-Arenes



Asymmetric dihydroxylation of β,β' -disubstituted enamides afforded chiral tertiary-alcohol-containing α -hydroxyaldehydes and 1,2-diols with high enantioselectivity (see scheme). This method was

applied to the total synthesis of the antifungal natural product (+)-tanikolide, as well as the synthesis of an intermediate en route to (*S*)-oxybutynin.

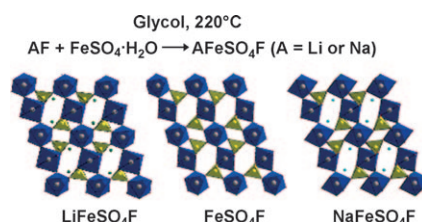
Asymmetric Catalysis

B. Gourdet, H. W. Lam* — 8733–8737

Catalytic Asymmetric Dihydroxylation of Enamides and Application to the Total Synthesis of (+)-Tanikolide



Single-phase tavorite, LiFeSO_4F , is crystallized in tetraethylene glycol at 220 °C to give an electrochemically highly active material. This route obviates the need for expensive ionic liquids and can be extended to the synthesis of NaFeSO_4F , whose structure solution, along with that of the parent framework FeSO_4F , provides understanding of ion mobility.



Lithium-Ion Batteries

R. Tripathi, T. N. Ramesh, B. L. Ellis, L. F. Nazar* — 8738–8742

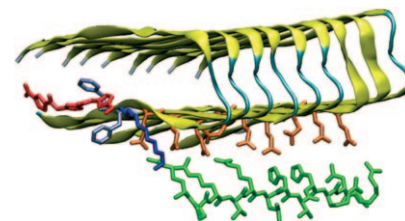
Scalable Synthesis of Tavorite LiFeSO_4F and NaFeSO_4F Cathode Materials



Hybrid Drugs

A. Müller-Schiffmann, J. März-Berberich, A. Andreyeva, R. Röncke, D. Bartnik, O. Brener, J. Kutzsche, A. H. C. Horn, M. Hellmert, J. Polkowska, K. Gottmann, K. G. Reymann, S. A. Funke, L. Nagel-Steger, C. Moriscot, G. Schoehn, H. Sticht, D. Willbold, T. Schrader, C. Korth* — 8743–8746

More than the sum of its parts: Novel hybrid compounds consisting of an organic β -sheet-breaking moiety and a signaling, D-enantiomeric A β -recognizing peptide moiety have been designed (see picture). The compounds, which were chemically synthesized and characterized by several techniques, combine rational design and drug selection from libraries and inhibit A β oligomerization and A β -induced synaptic pathology.



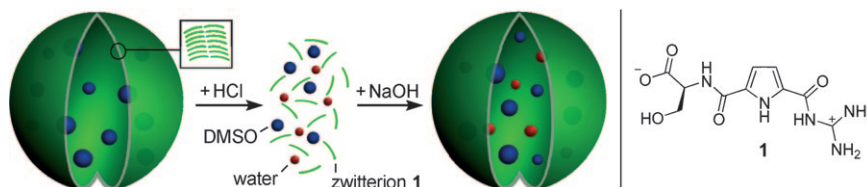
Combining Independent Drug Classes into Superior, Synergistically Acting Hybrid Molecules

Zwitterionic Vesicles

F. Rodler, J. Linders, T. Fenske, T. Rehm, C. Mayer, C. Schmuck* — 8747–8750



pH-Switchable Vesicles from a Serine-Derived Guanidiniocarbonyl Pyrrole Carboxylate Zwitterion in DMSO



Tightly closed: Zwitterion **1** forms vesicles that have an approximate size of 50 nm in DMSO solution. The vesicles can be opened and closed by the addition of either acid or base, as vesicle formation depends on the protonation state of

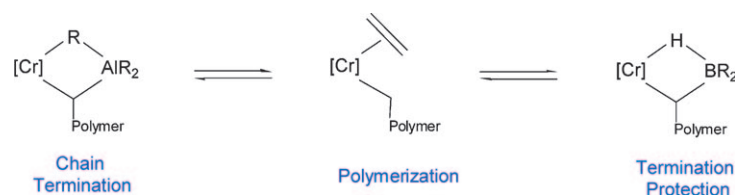
zwitterion **1** (see picture). The membrane permeability of the vesicles is surprisingly low: the encapsulated solvent does not exchange with the surrounding solution, even on a time scale of a few hundred milliseconds.

Olefin Polymerization

S. Mark, A. Kurek, R. Mülhaupt, R. Xu, G. Klatt, H. Köppel, M. Enders* — 8751–8754



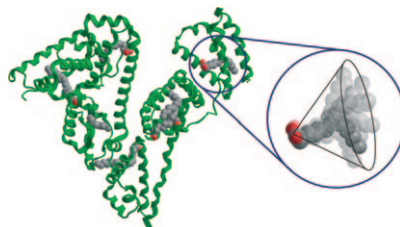
Hydridoboranes as Modifiers for Single-Site Organochromium Catalysts: From Low- to Ultrahigh-Molecular-Weight Polyethylene



Going to great lengths: The use of hydridoboranes as new modifiers for chromium-catalyzed olefin polymerization allows the preparation of polyethylene

with a precisely tunable ultrahigh molecular weight. This effect can be understood by a reversible protection of the active catalyst by the borane (see scheme).

Flexible on the outside: The functional structure of the transport protein in human blood, human serum albumin (HSA), was characterized by distance measurements with double electron–electron resonance (DEER) spectroscopy on spin-labeled fatty acids that are bound to HSA. The functional protein structure derived has a more rigid inner core, while the surface of the protein shows much greater structural flexibility.



Functional Protein Structure

M. J. N. Junk, H. W. Spiess,
D. Hinderberger* _____ 8755–8759

The Distribution of Fatty Acids Reveals the Functional Structure of Human Serum Albumin



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).

Sources

Product and Company Directory

You can start the entry for your company in “Sources” in any issue of *Angewandte Chemie*.

If you would like more information, please do not hesitate to contact us.

Wiley-VCH Verlag – Advertising Department

Tel.: 0 62 01 - 60 65 65

Fax: 0 62 01 - 60 65 50

E-Mail: MSchulz@wiley-vch.de

Service

Spotlight on Angewandte's
Sister Journals _____ 8554–8556

Keywords _____ 8760

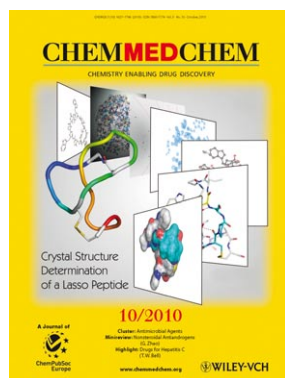
Authors _____ 8761

Preview _____ 8763

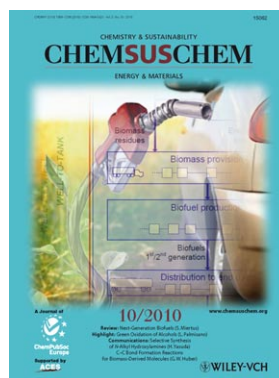
Check out these journals:



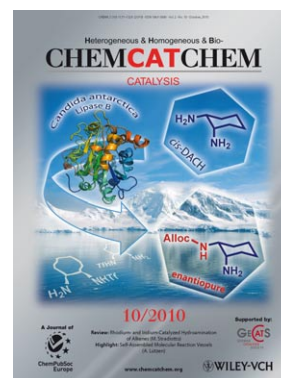
www.chemasianj.org



www.chemmedchem.org



www.chemsuschem.org



www.chemcatchchem.org