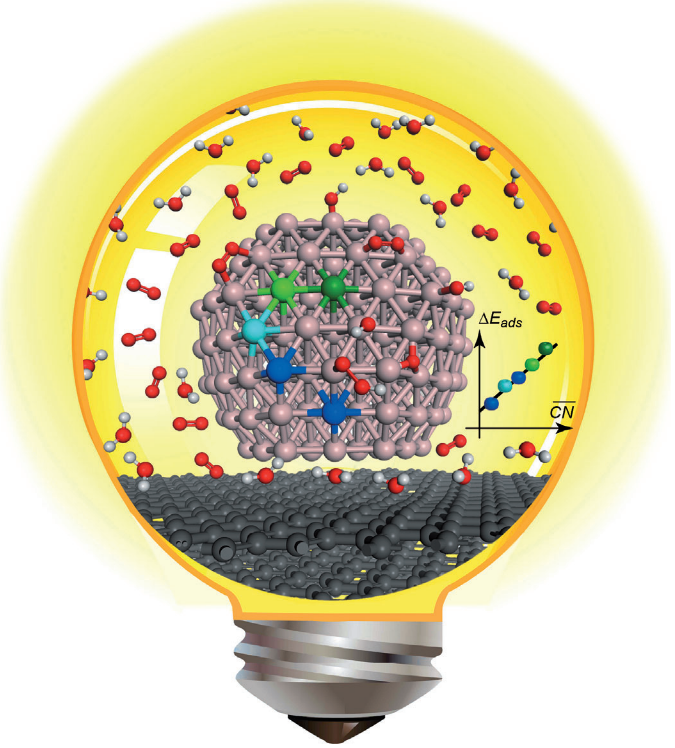
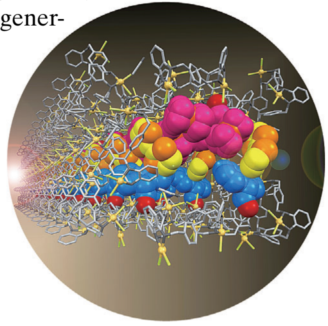
In heterogeneous catalysis ...

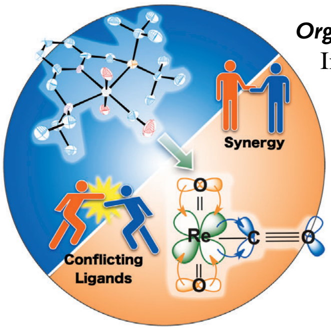


… and fuel-cell design, the fast and accurate prediction of chemical reactivity is paramount. Current theoretical models use electronic-structure-based descriptors with known limitations. D. Loffreda et al. demonstrate in their Communication on page 8316 ff. that the adsorption energetics of oxygenated species on various platinum nanoparticles and surfaces are linearly captured by a non-electronic, exact, and powerful descriptor: the generalized coordination number.



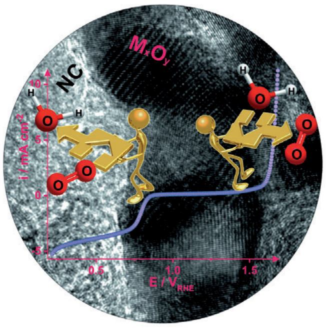
Molecular Arrangement

M. Shionoya et al. show in their Communication on page 8310 ff. the precisely controlled, simultaneous uptake of up to three different guest molecules within a single pore of a metal-macrocycle framework.



Organometallic Complexes

In metal complexes, π-donor oxo and π-acceptor carbonyl ligands rarely coexist. In their Communication on page 8320 ff., Abu-Omar et al. describe the first isolable dioxocarbonyl organometallic complex, in which the synergistic interaction between ligands stabilizes the pincer complex.



Dual-Function Catalysts

In their Communication on page 8508 ff., W. Schuhmann, M. Muhler et al. report bifunctional catalysts for oxygen reduction and oxygen evolution based on Co, Mn, and Ni oxides embedded in nitrogen-doped carbon.

How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 62 01–606-331
Telephone: (+49) 62 01–606-315

Reprints, E-Prints, Posters, Calendars:
Carmen Leitner
E-mail: chem-reprints@wiley-vch.de
Fax: (+49) 62 01–606-331
Telephone: (+49) 62 01–606-327

Copyright Permission:
Bettina Loycke
E-mail: rights-and-licences@wiley-vch.de
Fax: (+49) 62 01–606-332
Telephone: (+49) 62 01–606-280

Online Open:
Margitta Schmitt, Carmen Leitner
E-mail: angewandte@wiley-vch.de
Fax: (+49) 62 01–606-331
Telephone: (+49) 62 01–606-315

Subscriptions:
www.wileycustomerhelp.com
Fax: (+49) 62 01–606-184
Telephone: 0800 1800536 (Germany only)
+44(0) 1865476721 (all other countries)

Advertising:
Marion Schulz
E-mail: mschulz@wiley-vch.de
jspiess@wiley-vch.de
Fax: (+49) 62 01–606-550
Telephone: (+49) 62 01–606-565

Courier Services:
Boschstrasse 12, 69469 Weinheim

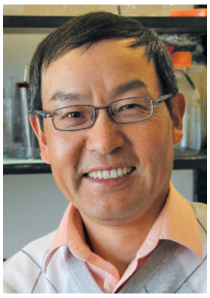
Regular Mail:
Postfach 101161, 69451 Weinheim

Angewandte Chemie International Edition is a journal of the Gesellschaft Deutscher Chemiker (GDCh), the largest chemistry-related scientific society in continental Europe. Information on the various activities and services of the GDCh, for example, cheaper subscription to *Angewandte Chemie International Edition*, as well as applications for membership can be found at **www.gdch.de** or can be requested from GDCh, Postfach 900440, D-60444 Frankfurt am Main, Germany.

GDCh
GESELLSCHAFT
DEUTSCHER CHEMIKER

Service

Author Profile



"My favorite molecule is DNA, because it is simple yet mysterious.
When I was eighteen I wanted to be a novelist …"
This and more about Yingfu Li can be found on page 8276.

News


J.-i. Yoshida


L. de Cola


S.-M. Peng


J. K. Barton


P. J. Stang

Books

Highlights

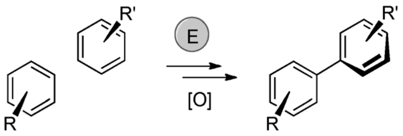
CO₂ Fixation

Catch me if you can: CO_2 is shown to reversibly bind to CN^-, forming the elusive cyanoformate anion, which is on the verge of breakdown. This is a significant finding with respect to the understanding of biological processes in enzymes and for molecular CO_2-based shuttle systems.

Minireviews

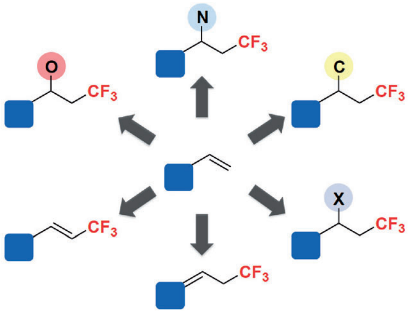
Natural Products

Enzymes crossing: The structural diversity and biomedical potential of biaryl natural products is tremendous. Equally intriguing are the biosynthetic tools nature has evolved to construct this privileged structural feature. This Minireview discusses selected examples of biocatalytic oxidative cross-coupling strategies in the biosynthesis of natural products.



Reviews

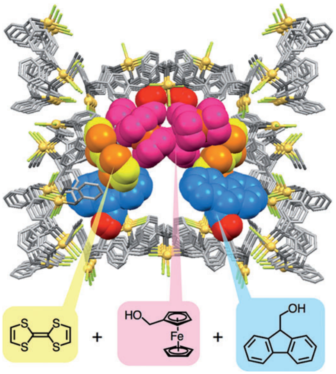
Trifluoromethylation



CF_3 and more: The trifluoromethyl group is the most widely studied fluorine-containing functional group. Many methods are available for the introduction of a trifluoromethyl group into organic molecules. This Review summarizes recent advances in the trifluoromethylation of alkenes with concomitant introduction of additional functional groups.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 11.738/10.206 (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.

Three different molecules in a single pore: TTF (tetrathiafulvalene), ferrocene, and fluorene are incorporated simultaneously on the pore surface of a porous crystalline metal–macrocycle framework (MMF), as revealed by single-crystal XRD analysis. The anchoring effects of hydrogen bonding with the hydroxy groups of the guest molecules and inter-guest cooperation and competition are critical control factors in the adsorption behavior of the guest molecules.

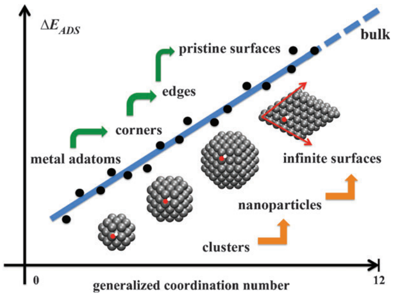


Molecular Arrangement

S. Tashiro, T. Umeki, R. Kubota,
M. Shionoya* ________ **8310 – 8315**

Simultaneous Arrangement of up to Three Different Molecules on the Pore Surface of a Metal–Macrocycle Framework: Cooperation and Competition

Frontispiece



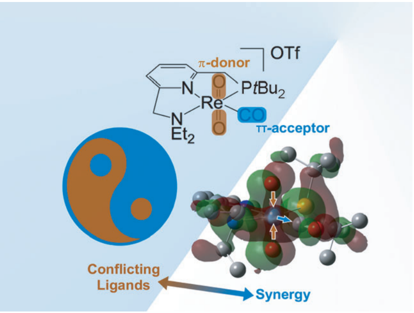
The trends in the adsorption energies of oxygen- and hydrogen-containing adsorbates on various platinum nanoparticles and extended surfaces are analyzed. By means of generalized coordination numbers, it is possible to unify the trends among dissimilar structures and sizes. Adsorption energies for terraces, edges, corners, and adatoms and finite-size effects could be accurately described.

Nanotechnology

F. Calle-Vallejo, J. I. Martínez,
J. M. García-Lastra, P. Sautet,
D. Loffreda* ________ **8316 – 8319**

Fast Prediction of Adsorption Properties for Platinum Nanocatalysts with Generalized Coordination Numbers

Front Cover



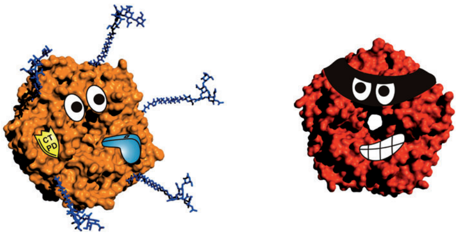
The best of both worlds! The synthesis of $[(PNN)Re(CO)(O)_2]$ marks the first isolable dioxo carbonyl organometallic complex. These species have previously only been identified in transient states, as they feature electronically conflicting ligands. DFT calculations indicate a synergistic relationship between these ligands and the metal center in this novel rhenium pincer complex.

Organometallics

M. G. Mazzotta, K. R. Pichaandi,
P. E. Fanwick,
M. M. Abu-Omar* ________ **8320 – 8322**

Concurrent Stabilization of π-Donor and π-Acceptor Ligands in Aromatized and Dearomatized Pincer $[(PNN)Re(CO)(O)_2]$ Complexes

Inside Back Cover



Cholera versus cholera: The inhibition of multivalent protein/carbohydrate interactions between toxins and glycolipids in cell membranes can prevent the toxins from entering cells. The site-specific modification of a protein scaffold, matched in both size and valency to the target toxin, led to a multivalent inhibitor with an IC_{50} value of 104 pM for the cholera toxin B-subunit.

Multivalent Inhibitors

VIP

T. R. Branson, T. E. McAllister,
J. Garcia-Hartjes, M. A. Fascione,
J. F. Ross, S. L. Warriner, T. Wennekes,
H. Zuilhof, W. B. Turnbull* **8323 – 8327**

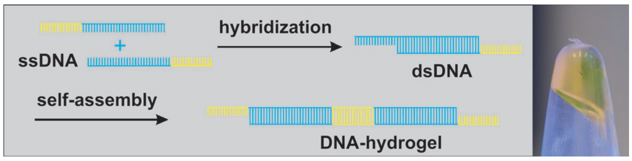
A Protein-Based Pentavalent Inhibitor of the Cholera Toxin B-Subunit

Inside Cover

DNA Hydrogels

T. Nöll, H. Schönherr, D. Wesner,
M. Schopferer, T. Paululat,*
G. Nöll* ________ 8328 – 8332

Construction of Three-Dimensional DNA Hydrogels from Linear Building Blocks

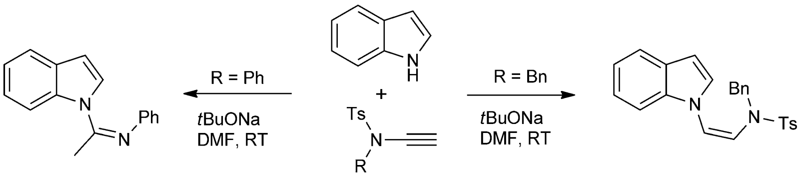


Genetic jelly: A 3D DNA hydrogel was generated by self-assembly of short linear double-stranded DNA (dsDNA) building blocks equipped with sticky ends. The supramolecular structures comprising the highly thermoresponsive hydrogel were studied with diffusion-ordered NMR spectroscopy (DOSY NMR), rheology, and atomic force microscopy (AFM). At room temperature, densely packed structures of entangled chains, which are also expected to contain multiple interlocked rings, were observed.

Synthetic Methods

A. Hentz, P. Retailleau, V. Gandon,
K. Cariou, R. H. Dodd* ____ 8333 – 8337

Transition-Metal-Free Tunable Chemoselective N Functionalization of Indoles with Ynamides



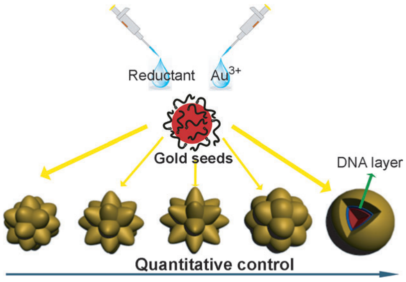
Two birds with one stone: Under basic reaction conditions, two distinct manners of functionalizing the nitrogen atom of indoles with ynamides are reported. Unsubstituted *N*-tosyl-*N*-alkyl ynamides undergo addition at the β-position to yield (*Z*)-2-indolo-etheneamide with complete regioselectivity, whereas *N*-phenyl and/or *N*-carboxyl ynamides undergo addition at the α-position, albeit with the concomitant loss of the electron-withdrawing group.

Gold Nanoparticles

J. Shen, L. Xu, C. Wang, H. Pei, R. Tai,
S. Song, Q. Huang, C. Fan,*
G. Chen* ________ 8338 – 8342

Dynamic and Quantitative Control of the DNA-Mediated Growth of Gold Plasmonic Nanostructures

A heart of gold: A quantitative approach to intercept the evolution of size, surface morphology, and the optical properties of Au plasmonic nanostructures is demonstrated by dynamic control of the DNA-mediated growth. The structural parameters of these nanostructures correlate well with their optical properties, obtained from small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM).

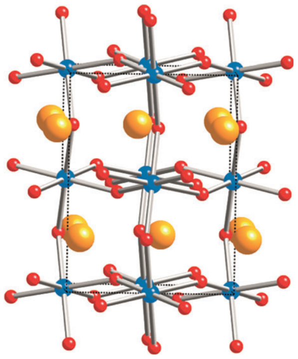


Materials Synthesis

A. Sinclair, J. A. Rodgers, C. V. Topping,
M. Míšek, R. D. Stewart, W. Kockelmann,
J.-W. G. Bos, J. P. Attfield* _ 8343 – 8347

Synthesis and Properties of Lanthanide Ruthenium(III) Oxide Perovskites

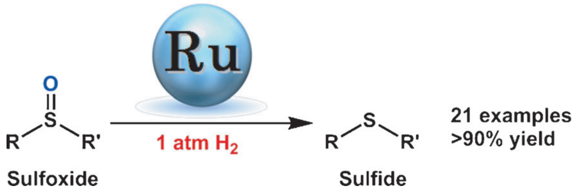
Putting the squeeze on Ru: An extensive series of new $LnRuO_3$ perovskites has been synthesized at high pressure. They are ruthenium deficient, with compositions close to $LnRu_{0.9}O_3$, and stabilize ruthenium(III), which has not been previously well characterized in oxides. They adopt orthorhombic perovskite superstructures in which strong spin-orbit coupling leads to tetragonal compression of the RuO_6 octahedra and Mott insulator behavior.



Heterogeneous Catalysis

T. Mitsudome, Y. Takahashi, T. Mizugaki, K. Jitsukawa, K. Kaneda* ___ **8348–8351**

Hydrogenation of Sulfoxides to Sulfides under Mild Conditions Using Ruthenium Nanoparticle Catalysts

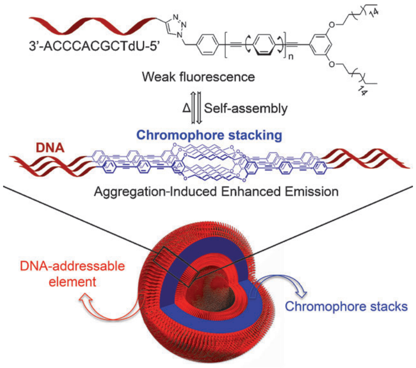


Ru nanoparticles supported on TiO_2 promote the selective hydrogenation of various functionalized sulfoxides at atmospheric H_2 pressure. The corresponding sulfides are obtained in excellent yields. The redox ability of Ru nanoparticles plays a crucial role in this hydrogenation reaction.

DNA Nanostructures

S. K. Albert, H. V. P. Thelu, M. Golla, N. Krishnan, S. Chaudhary, R. Varghese* ___ **8352–8357**

Self-Assembly of DNA–Oligo-(*p*-phenylene-ethynylene) Hybrid Amphiphiles into Surface-Engineered Vesicles with Enhanced Emission

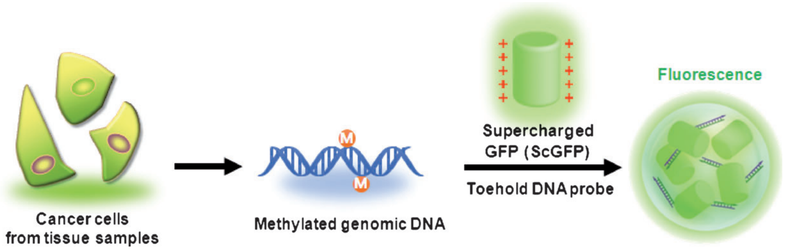


Surface engineering: DNA–oligomer hybrid amphiphiles self-assemble into surface-functionalized vesicles with enhanced emission. Sequence-specific DNA hybridization allows the assembly of functional molecules onto the surface of the vesicle, providing a unique opportunitie to study the distance-dependent electronic interaction of chromophore stacks with other molecules.

Bioanalysis

C. Y. Lei, Y. Huang, Z. Nie,* J. Hu, L. J. Li, G. Y. Lu, Y. T. Han, S. Z. Yao **8358–8362**

A Supercharged Fluorescent Protein as a Versatile Probe for Homogeneous DNA Detection and Methylation Analysis



Supercharged protein sensor: Taking supercharged green fluorescent protein (ScGFP) as the signal reporter, a simple turn-on homogeneous method for DNA detection and methylation analysis of cancer tissue samples has been developed based on the polyionic nanoscale complex of ScGFP/DNA and toehold-mediated strand displacement.

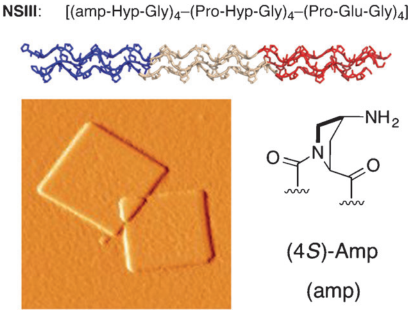
Hybrid Nanoparticles

J. Spadavecchia, E. Apchain, M. Albéric, E. Fontan, I. Reiche* ___ **8363–8366**

One-Step Synthesis of Collagen Hybrid Gold Nanoparticles and Formation on Egyptian-like Gold-Plated Archaeological Ivory

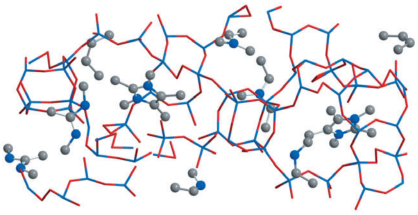
Time matters: From purple to gold: Collagen hybrid AuNPs have been synthesized by a simple one-step method. The determined mechanism explains the formation of AuNPs found in purple stains on formerly gilded archaeological ivories. This finding can serve as a new criterion for authenticating ancient gold-plated ivories that cannot be identified in a non-invasive way.

Structurally Uniform Nanosheets



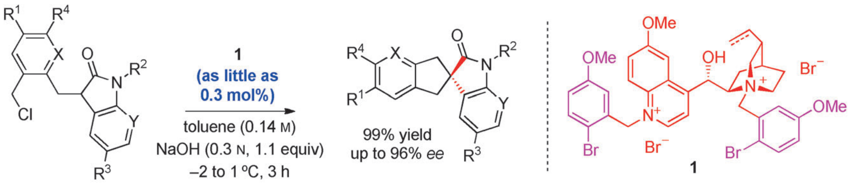
Amp-ed up self-assembly: A triblock collagen-mimetic peptide, NSIII, self-assembles into a monodisperse population of nanosheets of defined size and shape. The experimental evidence suggests that the presence of 4*S*-aminoproline (amp) in the peptide sequence imposes stereoelectronic constraints on the conformation of the triple helix that restricts the size distribution of the resultant nanosheets.

Zeolite Synthesis



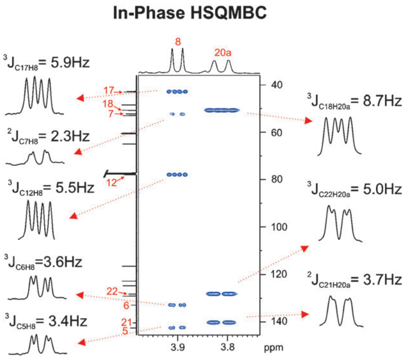
Experimental validation has been realized of a computational method that is able to screen a large number of organic structure-directing agents (OSDAs). The study shows that the method is able to successfully predict OSDAs for a specified framework by using known chemical reactions, and yield predicted occupancies that are measured in the products (see the calculated structure of STW with occluded pentamethylimidazolium).

Phase-Transfer Catalysis



A doubly positive development: *N*,*N*′-Disubstituted cinchona alkaloids were found to be highly efficient phase-transfer catalysts for the assembly of stereogenic quaternary centers. In comparison to traditional cinchona-alkaloid phase-transfer catalysts they afforded substantial improvements in enantioselectivity and reactivity in intramolecular spirocyclization reactions at catalyst loadings as low as 0.3 mol% under mild conditions (see example).

NMR Spectroscopy

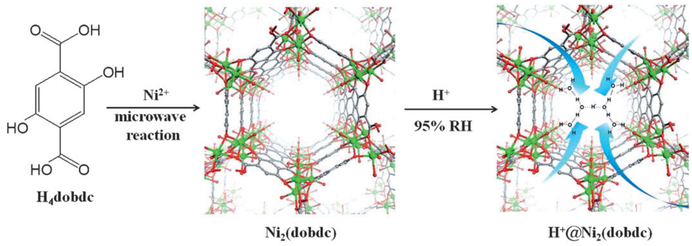


Clean spectra: A general NMR approach to provide pure in-phase (PIP) multiplets in heteronuclear correlation experiments is described. The implementation of a *z*-filter suppresses unwanted anti-phase contributions that usually distort the multiplet pattern of cross-peaks. The clean pattern obtained is suitable for a direct extraction of coupling constants and for a peak-fitting process from a reference signal.

Proton Conducting Materials

W. J. Phang, W. R. Lee, K. Yoo, D. W. Ryu,
B. Kim, C. S. Hong* ______ **8383 – 8387**

pH-Dependent Proton Conducting Behavior in a Metal–Organic Framework Material

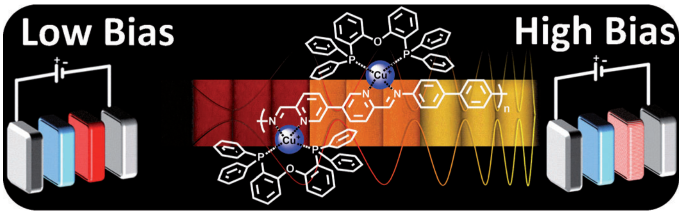


A fuel cell candidate: Treatment of the metal–organic framework [Ni_2(dobdc)] with sulfuric acid afforded a new proton conducting framework, H^+@Ni_2(dobdc). This acidified MOF displays one of the highest proton conductivities reported for MOFs and is characterized by a exceptionally low activation energy of proton transfer.

Metallopolymers

D. Asil, J. A. Foster, A. Patra, X. de Hatten,
J. del Barrio, O. A. Scherman,
J. R. Nitschke,*
R. H. Friend* ______ **8388 – 8391**

Temperature- and Voltage-Induced Ligand Rearrangement of a Dynamic Electroluminescent Metallopolymer

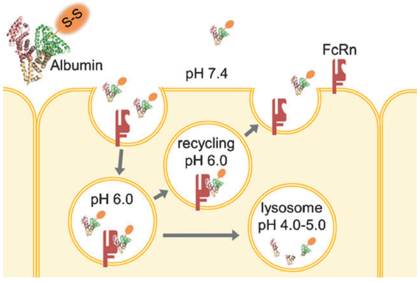


Tunable LECs: A dynamic-covalent metal-containing polymer which can reversibly rearrange its structure in response to high temperature or electric field is reported. In solution, the polymers form heat-set gels at high temperatures. When incorporated into light-emitting electrochemical cells (LECs), the wavelength of emission depends on the applied voltage.

Bio-reduction

L. Brülisauer, G. Valentino, S. Morinaga,
K. Cam, J. Thostrup Bukrinski,
M. A. Gauthier,
J.-C. Leroux* ______ **8392 – 8396**

Bio-reduction of Redox-Sensitive Albumin Conjugates in FcRn-Expressing Cells

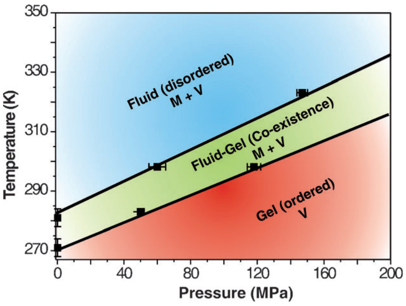


Disulfide-containing IgG-, Fc-, or albumin-based prodrugs that rely on FcRn-trafficking by endothelial cells for prolonged circulation in the body might be hampered by premature bio-reduction processes during FcRn-recycling events. A detailed bio-reduction analysis of redox-sensitive albumin conjugates in two FcRn-expressing cell lines has been performed. New insights are provided to improve the performance of these classes of therapeutics.

Prebiotic Cell Membranes

S. Kapoor, M. Berghaus, S. Suladze,
D. Prumbaum, S. Grobelny, P. Degen,
S. Raunser, R. Winter* ______ **8397 – 8401**

Prebiotic Cell Membranes that Survive Extreme Environmental Pressure Conditions



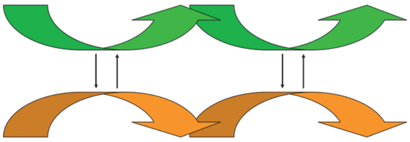
Prebiotic membranes under high pressure: Prebiotic membranes not only withstand extreme temperatures, but also serve as robust models of protocells operating in extreme pressure environments. Pressure not only increases the stability of vesicular systems but also limits their flexibility and permeability to solutes, while keeping the membrane in an overall fluid-like and thus functional state under deep-sea-like conditions.

DNA Nanotechnology

Z. Nie,* P. F. Wang, C. Tian,
C. Mao* ________ 8402 – 8405

Synchronization of Two Assembly Processes To Build Responsive DNA Nanostructures

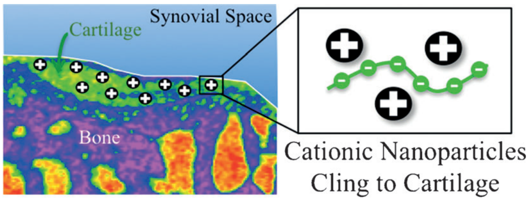
A ladder to higher places: A strategy to synchronize otherwise independent self-assembly processes (represented schematically in green and orange) enabled the assembly of complex DNA nanostructures. As a proof-of-concept, ladder-like and ringlike DNA nanostructures were assembled.



Nanoparticles for Imaging Cartilage

J. D. Freedman, H. Lusic, B. D. Snyder,
M. W. Grinstaff* ________ 8406 – 8410

Tantalum Oxide Nanoparticles for the Imaging of Articular Cartilage Using X-Ray Computed Tomography: Visualization of Ex Vivo/In Vivo Murine Tibia and Ex Vivo Human Index Finger Cartilage

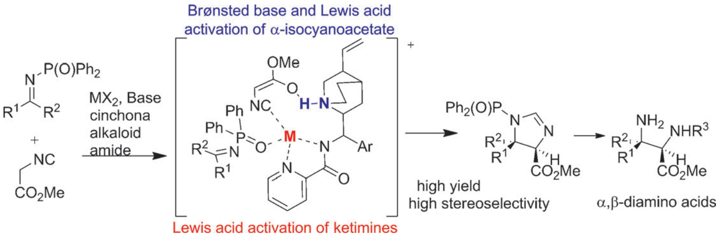


Cartilage imaging: Tantalum oxide (Ta_2O_5) nanoparticles serve as X-ray contrast media for imaging articular cartilage by microcomputed tomography. The cationic nanoparticles are attracted to the anionic glycosaminoglycans in the cartilage tissue.

Asymmetric Synthesis

M. Hayashi, M. Iwanaga, N. Shiomi,
D. Nakane, H. Masuda,
S. Nakamura* ________ 8411 – 8415

Direct Asymmetric Mannich-Type Reaction of α-Isocyanoacetates with Ketimines using Cinchona Alkaloid/Copper(II) Catalysts

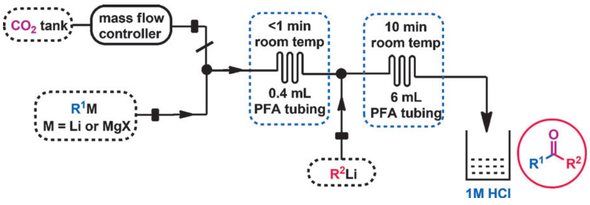


The enantioselective direct Mannich-type reaction of ketimines with α-isocyanoacetates has been developed. Excellent yields and enantioselectivities were observed for the reaction of various ketimines and α-isocyanoacetates using cinchona alkaloid/Cu(OTf)$_2$ and a base. Both enantiomers of the products could be obtained by using pseudoenantiomeric chiral catalysts. This process offers an efficient route for the synthesis of α,β-diamino acids.

Synthetic Methodology

J. Wu, X. Yang, Z. He, X. Mao,
T. A. Hatton,*
T. F. Jamison* ________ 8416 – 8420

Continuous Flow Synthesis of Ketones from Carbon Dioxide and Organolithium or Grignard Reagents

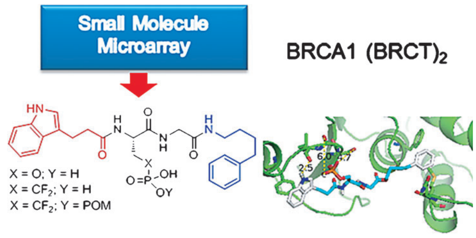


Known chemistry in flow: The continuous flow synthesis of ketones using CO_2 and organolithium or Grignard reagents exhibits significant advantages over conventional batch conditions. Undesired symmetric ketone and alcohol by-products are suppressed and an unprecedented solvent-dependence of the organolithium reactivity was used to achieve the desired selectivity.

Protein–Protein Interaction

Z. Na, S. Pan, M. Uttamchandani, S. Q. Yao* ———— **8421 – 8426**

Discovery of Cell-Permeable Inhibitors That Target the BRCT Domain of BRCA1 Protein by Using a Small-Molecule Microarray

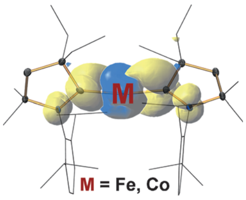


Array and break: By using microarray-based screening platforms the first cell-permeable small-molecule-like protein–protein interaction inhibitors against BRCA1 were identified (see picture). These compounds possess potent in vitro inhibitory activity against BRCA1 $(BRCT)_2$. In cancer cells they disrupt BRCA1 $(BRCT)_2$–protein interactions, and in combination with Olaparib, cause cell death synergistically by activation of the apoptosis pathway.

Low-Coordinate Complexes

G. Ung, J. Rittle, M. Soleilhavoup, G. Bertrand,* J. C. Peters* — **8427 – 8431**

Two-Coordinate Fe^0 and Co^0 Complexes Supported by Cyclic (alkyl)(amino)carbenes

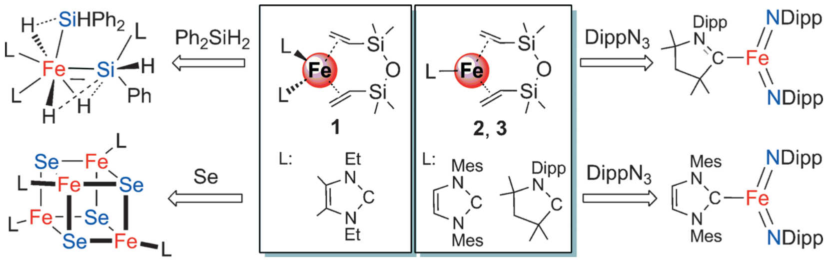


A delightfully lack of coordination: The CAAC [CAAC = cyclic (alkyl)(amino)carbene] family of carbene ligands allow access to the first examples of two-coordinate formal Fe^0 and Co^0 $[M(CAAC)_2]$ complexes. These compounds are prepared by reduction of their corresponding two-coordinate cationic Fe^I and Co^I precursors. Their stability arises from the strong σ-donating and π-accepting properties of the supporting CAAC ligands, as well as steric protection.

Iron(0) Reagents

H. Zhang, Z. Ouyang, Y. Liu, Q. Zhang, L. Wang, L. Deng* ———— **8432 – 8436**

(Aminocarbene)(Divinyltetramethyldisiloxane)Iron(0) Compounds: A Class of Low-Coordinate Iron(0) Reagents

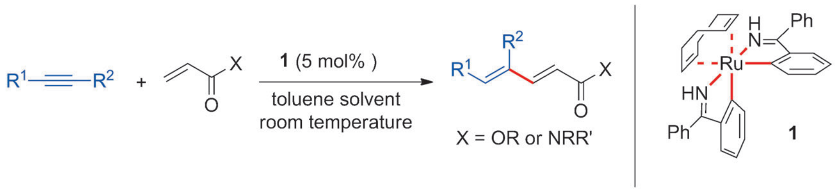


The low-down on iron: The use of carbene ligands, both NHC and CAAC, enables the access of low-coordinate iron(0) alkene compounds **1**–**3** that can effectively deliver their low-coordinate iron(0) fragments to perform redox reactions with hydrosilanes, chalcogen elements, and organic azides.

Homogeneous Catalyst

J. Zhang, A. Ugrinov, Y. Zhang,* P. Zhao* ———— **8437 – 8440**

Exploring Bis(cyclometalated) Ruthenium(II) Complexes as Active Catalyst Precursors: Room-Temperature Alkene–Alkyne Coupling for 1,3-Diene Synthesis

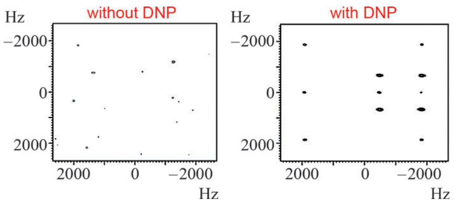


C–H activation: The ruthenium catalyst **1** promoted coupling between acrylic esters and amides with internal alkynes to form 1,3-diene products at room temperature. A proposed catalytic cycle involves C–C bond formation by oxidative cyclization, β-hydride elimination, and C–H bond reductive elimination.

^{19}F NMR Spectroscopy

C. George,
N. Chandrakumar* ________ **8441 – 8444**

Chemical-Shift-Resolved ^{19}F NMR Spectroscopy between 13.5 and 135 MHz: Overhauser–DNP-Enhanced Diagonal Suppressed Correlation Spectroscopy

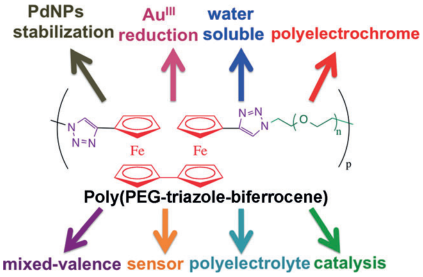


Overhauser–DNP-enhanced homonuclear 2D ^{19}F correlation spectroscopy with diagonal suppression is presented for small molecules in solution at moderate fields (13.5–135 MHz; DNP = dynamic nuclear polarization). At these relatively low fields, structural information is nevertheless accessible without a sensitivity penalty. This powerful general approach avoids the special requirements of high-field ^{19}F NMR spectroscopy.

Biferrocene Polymers

C. Deraedt, A. Rapakousiou, Y. Wang,
L. Salmon, M. Bousquet,
D. Astruc* ________ **8445 – 8449**

Multifunctional Redox Polymers: Electrochrome, Polyelectrolyte, Sensor, Electrode Modifier, Nanoparticle Stabilizer, and Catalyst Template

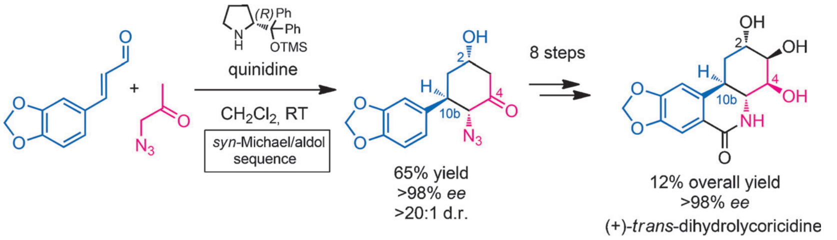


Very versatile: New metallopolymers were designed and prepared by “click” polycondensation between bis(ethynyl)-biferrocene and poly(ethylene glycol) (PEG400 and PEG1000) fragments. These can be used for multiple functions and uses including the improvement of water solubility and biocompatibility, the stabilization of Pd and Au nanoparticles, in catalysis, electrode derivatization, and sensing, and as a polyelectrochrome and polyelectrolyte.

Natural Products

J. McNulty,*
C. Zepeda-Velázquez ________ **8450 – 8454**

Enantioselective Organocatalytic Michael/Aldol Sequence: Anticancer Natural Product (+)-*trans*-Dihydrolycoricidine



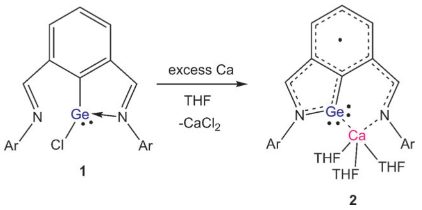
Taking steps: A stepwise organocatalytic Michael addition/aldol sequence is described involving secondary-amine-catalyzed regioselective addition of azidoacetone to cinnamaldehyde derivatives followed by intramolecular aldolization. Application of this route to aminocyclitols is demonstrated by a short, asymmetric synthesis of the anticancer natural product (+)-*trans*-dihydrolycoricidine.

Group 14 Chemistry

S.-P. Chia, E. Carter, H.-W. Xi, Y. Li,
C.-W. So* ________ **8455 – 8458**

Group II Metal Complexes of the Germylidendiide Dianion Radical and Germylidenide Anion

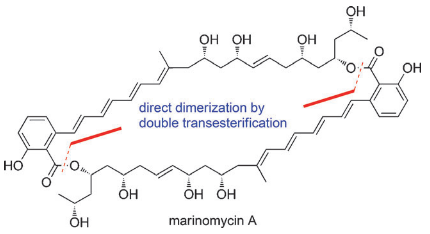
Germanium heterocycle: The reaction of **1** with excess calcium in THF at room temperature afforded **2** (see picture). X-ray crystallography and theoretical studies show that the germanium center in **2** has two lone pairs of electrons and that the radical is delocalized over the germanium-containing heterocycle.



Natural Product Synthesis

T. Nishimaru, M. Kondo, K. Takeshita,
K. Takahashi, J. Ishihara,
S. Hatakeyama* ________ 8459 – 8462

Total Synthesis of Marinomycin A Based on a Direct Dimerization Strategy

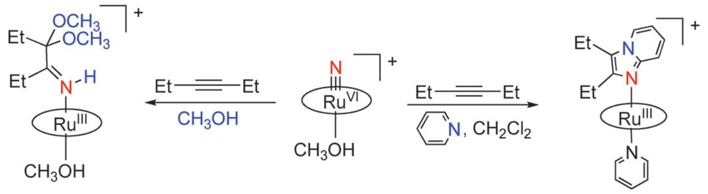


Seeing double: The asymmetric total synthesis of (+)-marinomycin A, a 44-membered macrodiolide antitumor agent and antibiotic, is reported. The key features of the synthesis include the highly convergent stereocontrolled construction of the monomeric hydroxy salicylate starting from asymmetric epoxidation of the σ-symmetrical dialkenyl carbinol, and an unprecedented direct dimerization through NaHMDS-promoted double transesterification.

Reaction Mechanisms

W. L. Man, J. Xie, P. K. Lo, W. W. Y. Lam,
S. M. Yiu, K. C. Lau,
T. C. Lau* ________ 8463 – 8466

Functionalization of Alkynes by a (Salen)ruthenium(VI) Nitrido Complex

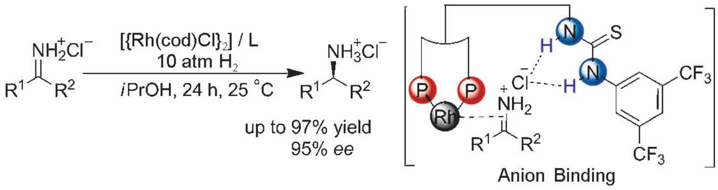


Alkyne nitrogenation: Reaction of a (salen)ruthenium(VI) nitrido complex with various alkynes in different solvents affords novel (salen)ruthenium(III) imine complexes, which have been evidenced by their X-ray structures. This reaction opens a new nitrogenation pathway for preparing N-containing materials.

Asymmetric Catalysis

Q. Zhao, J. Wen, R. Tan, K. Huang,
P. Metola, R. Wang,* E. V. Anslyn,*
X. Zhang* ________ 8467 – 8470

Rhodium-Catalyzed Asymmetric Hydrogenation of Unprotected NH Imines Assisted by a Thiourea

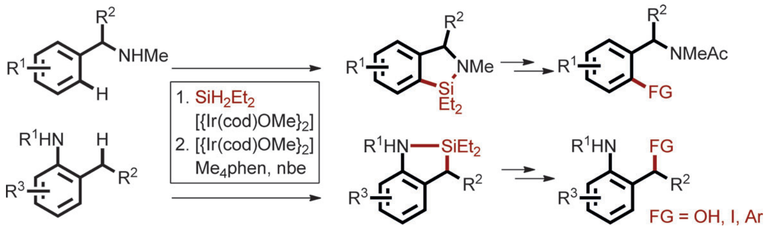


In a bind: A bis(phosphine)-thiourea ligand was successfully used in the rhodium-catalyzed asymmetric hydrogenation of unprotected iminium salts. Control experiments and ^{1}H NMR studies implied that the anion binding between the thiourea and chloride ions was involved in the mechanism. Deuteration experiments proved that the hydrogenation proceeded through a pathway consistent with an imine.

C–H Activation

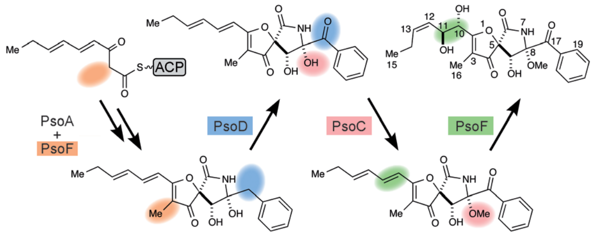
Q. Li, M. Driess,
J. F. Hartwig* ________ 8471 – 8474

Iridium-Catalyzed Regioselective Silylation of Aromatic and Benzylic C–H Bonds Directed by a Secondary Amine



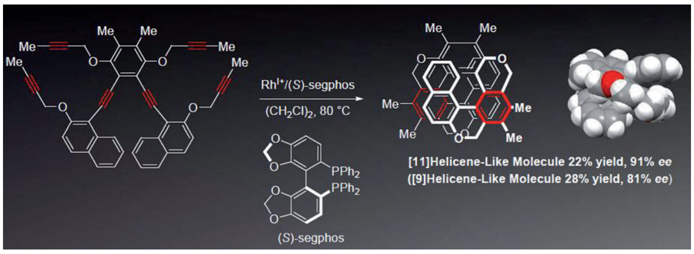
A ’SiN’ch: In the title reaction of benzylamines or anilines, (hydrido)silyl amines are generated in situ which undergo selective silylation at the C–H bond γ to the amino group. The silylation products can be further functionalized through oxidation, halogenation, and cross-coupling reactions. cod = 1,5-cyclooctadiene, nbe = norbornene.

Enzyme Catalysis



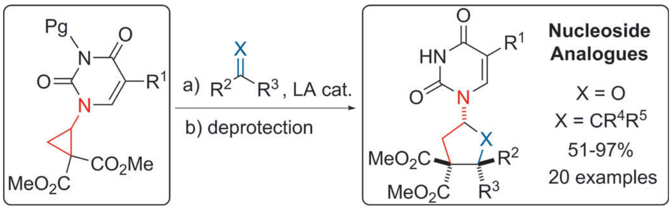
A maze: Pseurotins are a family of structurally related bioactive natural products from Aspergilli. Through genetic and biochemical studies, the biosynthetic pathway for the formation of azaspirene, synerazol, and pseurotin A/D have been elucidated, and reveal the combinatorial nature of their biosyntheses. PsoF was identified as bifunctional epoxidase methyltransferase enzyme, thus providing the first example of a trans-acting polyketide C-methyltransferase.

Helical Structures



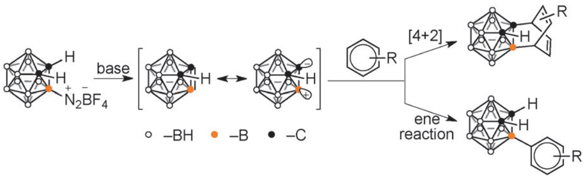
Link up: The enantioselective synthesis of completely *ortho*-fused [9]- and [11]helicene-like molecules has been achieved through a rhodium-mediated, intramolecular, double [2+2+2] cycloaddition of phenol- or 2-naphthol-linked hexaynes. The crystal structures and photophysical properties of these molecules have also been disclosed.

Synthetic Methods



(Carbo)nucleoside derivatives constitute an important class of pharmaceuticals. The first synthesis of thymine-, uracil-, and 5-fluorouracil-substituted diester donor–acceptor cyclopropanes and their use in indium- and tin-catalyzed [3+2] annulations with aldehydes, ketones, and enol ethers is described. The method gave access to (carbo)nucleoside analogues in only a few steps and will be highly useful for the synthesis of libraries of bioactive compounds.

Cage Compounds

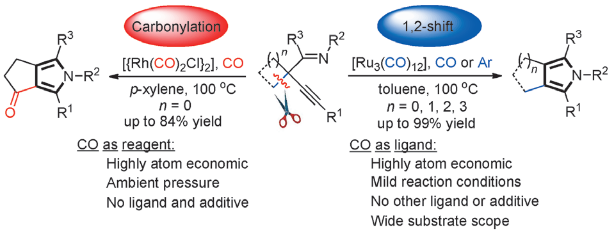


Rattle the cage: 1,3-Dehydro-*o*-carborane featuring a cage, with C–B bonds having multiple bonding characters, has been efficiently generated by reaction of 3-diazonium-*o*-carborane tetrafluoroborate with non-nucleophilic bases. The resulting reactive intermediate can undergo Diels–Alder and aromatic ene reactions with a series of arenes (see scheme).

Pyrrole Synthesis

G.-Q. Chen, X.-N. Zhang, Y. Wei,
X.-Y. Tang,* M. Shi* ______ **8492 – 8497**

Catalyst-Dependent Divergent Synthesis of Pyrroles from 3-Alkynyl Imine Derivatives: A Noncarbonylative and Carbonylative Approach

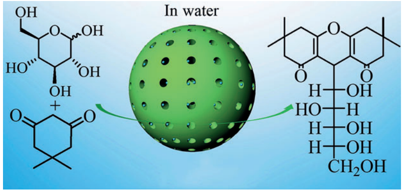


Carbonylation or not: A novel Ru^0- and Rh^I-catalyzed noncarbonylative and carbonylative synthesis of multisubstituted pyrroles from readily available 3-alkynyl imine derivatives has been developed. The key steps involve an oxidative addition and a 1,2-alkyl shift, respectively.

Mesoporous Polymeric Catalyst

F. Zhang,* C. Liang, X. Wu,
H. Li* ______ **8498 – 8502**

A Nanospherical Ordered Mesoporous Lewis Acid Polymer for the Direct Glycosylation of Unprotected and Unactivated Sugars in Water

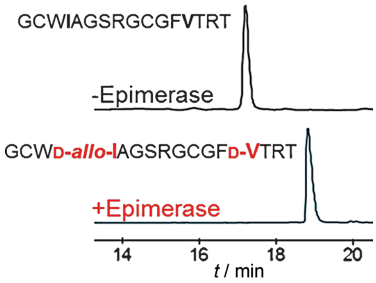


Xanthone glycosides from sugars: A novel nanospherical ordered mesoporous Lewis acid polymer was synthesized by functionalizing the mesoporous phenol-formaldehyde polymer with scandium triflate groups. The functionalized polymer showed good catalytic activity, selectivity, and recyclability in the C-glycosylation reaction between simple sugars and cyclohexane-1,3-dimedone in water.

Peptide Biosynthesis

B. I. Morinaka, A. L. Vagstad, M. J. Helf,
M. Gugger, C. Kegler, M. F. Freeman,
H. B. Bode, J. Piel* ______ **8503 – 8507**

Radical *S*-Adenosyl Methionine Epimerases: Regioselective Introduction of Diverse D-Amino Acid Patterns into Peptide Natural Products

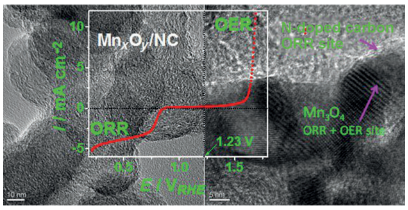


A radical change: Radical *S*-adenosyl methionine (SAM) epimerases is a new family of architecturally and functionally distinct bacterial enzymes. Three members from cyanobacteria were shown to introduce diverse D-amino acid patterns into all-L peptides. Their high regioselectivity, substrate promiscuity, and irreversible action provide interesting opportunities for peptide engineering.

Bifunctional Catalysts

J. Masa, W. Xia, I. Sinev, A. Zhao, Z. Sun,
S. Grützke, P. Weide, M. Muhler,*
W. Schuhmann* ______ **8508 – 8512**

Mn_xO_y/NC and Co_xO_y/NC Nanoparticles Embedded in a Nitrogen-Doped Carbon Matrix for High-Performance Bifunctional Oxygen Electrodes



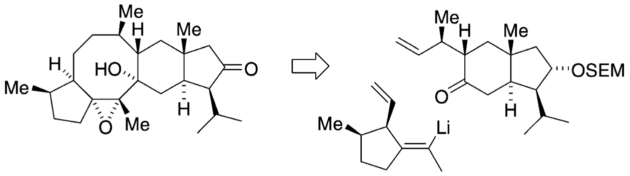
A dual finds its right setting: To improve the efficiency of metal–air batteries and unitized regenerative fuel-cell systems dual-function catalysts that can accomplish both water oxidation and oxygen reduction are required. Low-cost bifunctional catalysts based on Co, Mn, and Ni oxides embedded in N-doped carbon (NC) are synthesized and outperform Pt-, Ir- and, Ru-based catalysts.

Back Cover

Natural Product Synthesis

D. T. Hog, F. M. E. Huber, P. Mayer,
D. Trauner* ______________ **8513 – 8517**

The Total Synthesis of (−)-Nitidasin



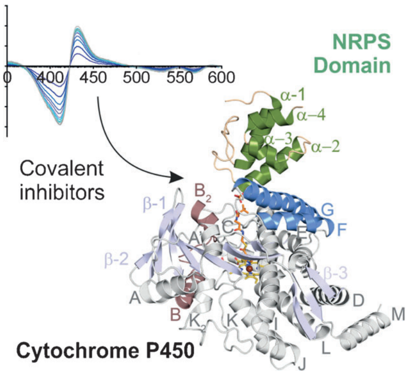
Put a ring on it: The first total synthesis of nitidasin, a complex sesterterpenoid with a 5-8-6-5 skeleton, is reported. It involves the addition of a tetrasubstituted alkenyl lithium compound to a *trans*-hydrindanone and an olefin metathesis to form a highly substituted eight-membered ring at an unexpected site. The absolute configuration of nitidasin was established with our highly stereoselective and convergent synthesis.

Protein–Protein Interactions

K. Haslinger, C. Brieke, S. Uhlmann,
L. Sieverling, R. D. Süssmuth,
M. J. Cryle* ______________ **8518 – 8522**

The Structure of a Transient Complex of a Nonribosomal Peptide Synthetase and a Cytochrome P450 Monooxygenase

Caught in the act: The structural characterization of a transient complex between the carrier protein (CP) domain of a nonribosomal peptide synthetase (NRPS) and a cytochrome P450 oxidase was made possible through the use of covalent inhibitor-type compounds. The structure reveals a novel binding site on the CP for such tailoring enzymes and suggests that the selectivity involves manipulation of the CP tertiary structure.



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).

This article is available online free of charge (Open Access).

This article is accompanied by a cover picture (front or back cover, and inside or outside).

The Very Important Papers, marked VIP, have been rated unanimously as very important by the referees.

The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.