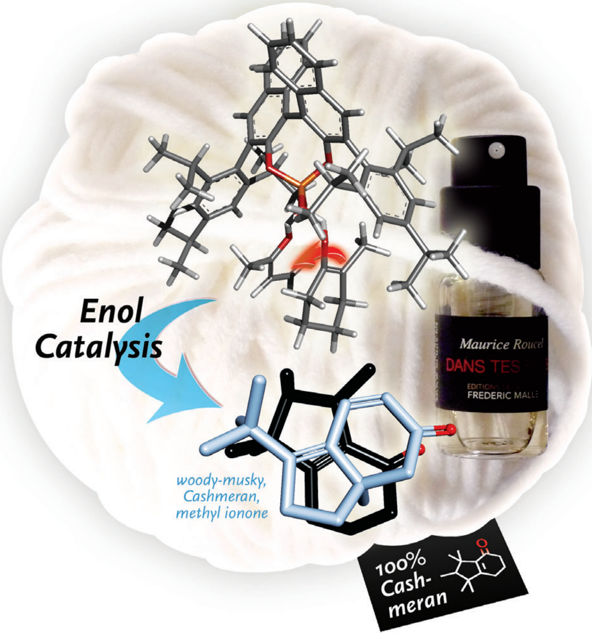
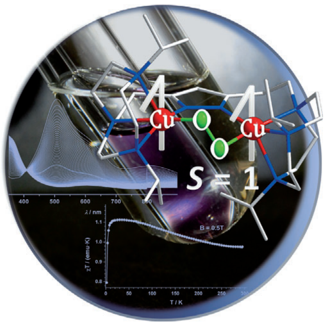
Cashmere Wood ...

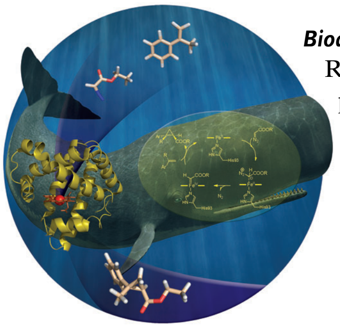


… is the term used for the typical odor of Cashmeran, which is found in perfumes, such as “Dans Tes Bras”. In their Communication on page 1960 ff., B. List, P. Kraft, and co-workers describe the design of novel Cashmeran odorants and their stereoselective synthesis through enol activation. The key transformation is a chiral phosphoric acid catalyzed Michael addition of enones to α-substituted ketones. The results grant insight into the structure–odor correlations of these odorants.



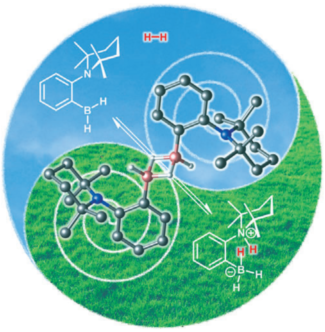
Biomimetic Copper Complexes

In their Communication on page 1738 ff, F. Meyer and co-workers prepare a copper peroxo complex. Constraining the Cu-O-O-Cu torsion angle to about 90° gives a snap shot of O_2 binding at biological type III dicopper sites.



Biocatalysis

R. Fasan et al. describe in their Communication on page 1744 ff. a rationally designed myoglobin catalyst that promotes the cyclopropanation of a range of aryl-substituted olefins with high catalytic activity and excellent diastereo- and enantioselectivity.



Hydrogen Splitting

The reactivity of an *ansa*-aminoborane, an intramolecular frustrated Lewis pair (FLP) with the smallest Lewis acidic boryl site (BH_2), towards H_2 is described by I. Pápai, T. Repo et al. in their Communication on page 1749 ff.

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Service

Author Profile

"I admire people who do more and talk less. If I could be anyone for a day, I would be a farmer and plant green vegetables ..."
This and more about Jingsong You can be found on page 1704.

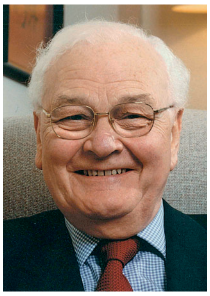
News

M. H. G. Prechtl

F. Rosei

T. Gunnlaugsson

Obituaries



Jack Lewis passed away at the age of 86 on July 17, 2014. He will be remembered as one of the father figures of modern inorganic chemistry and for his pioneering work in the area of metal–metal bonded complexes. He developed the field of transition-metal carbonyl clusters, including the chemistry of ruthenium and osmium carbonyl compounds and other mixed-metal cluster systems.

Books

Separation of Enantiomers — Matthew H. Todd — *reviewed by R. Kellogg* — **1707**

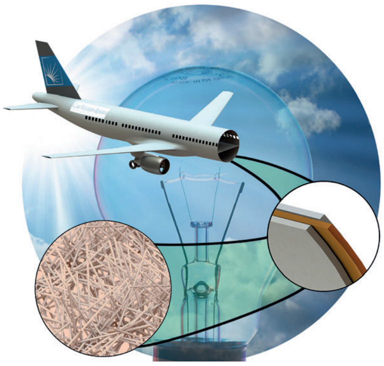
Minireviews

Thermoelectric Polymers

B. T. McGrail, A. Sehirlioglu,
E. Pentzer* — **1710 – 1723**

Polymer Composites for Thermoelectric Applications

Energy budget: This Minireview summarizes recently reported polymer composites that show a thermoelectric (TE) effect and thus have potential application as thermoelectric generators and Peltier coolers. Composites with inorganic and organic additives in conjugated and insulating polymer matrices are covered, as well as the techniques needed to characterize their TE properties.



Reviews

Rare-Earth-Metal Hydrides

W. Fegler, A. Venugopal, M. Kramer,
J. Okuda* — **1724 – 1736**

Molecular Rare-Earth-Metal Hydrides in Non-Cyclopentadienyl Environments

Beyond Cp: Molecular hydrides of rare-earth metals play an important role as homogeneous catalysts and as models of solid-state interstitial hydrides. This Review provides an overview of rare-earth-metal hydride complexes (without cyclopentadienyl ligands), with emphasis on the structural motifs and the effect of cationic charges on reactivity.

Communications

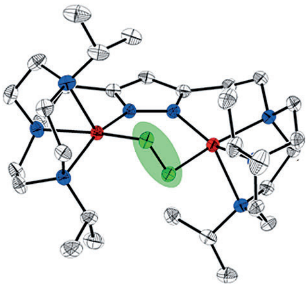
Biomimetic Copper–O_2 Chemistry

N. Kindermann, E. Bill, S. Dechert,
S. Demeshko, E. J. Reijerse,
F. Meyer* — **1738 – 1743**

A Ferromagnetically Coupled ($S = 1$) Peroxodicopper(II) Complex

Frontispiece

Stuck in the middle with Cu: Rational ligand design results in a μ-η^1:η^1-peroxo dicopper(II) complex whose Cu-O-O-Cu torsion is constrained to around 90°, allowing a sizeable ferromagnetic coupling between the Cu^{II} ions and a triplet ground state. The complex is a snapshot of the initial stages of O_2 binding at biological type III dicopper sites (Cu red, O green).



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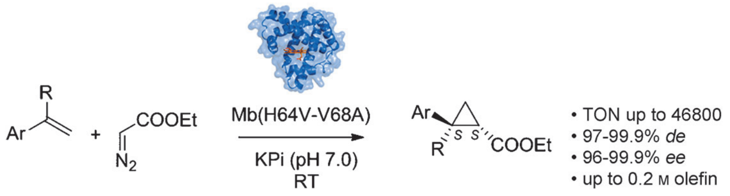
Biocatalysis

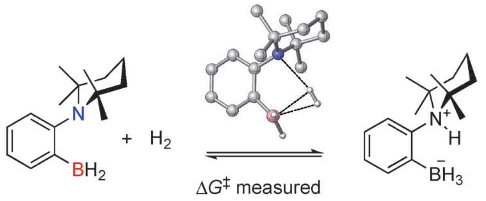
Inside Back Cover



The mediator: A rationally designed myoglobin (Mb) catalyst is capable of promoting the cyclopropanation of a range of aryl-substituted olefins with high catalytic activity and excellent diastereo- and enantioselectivity. These studies define myoglobin as a promising and robust scaffold for mediating carbene-transfer reactions.

Hydrogen Splitting

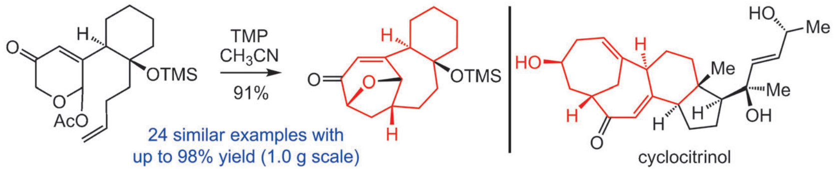
Back Cover



As simple as that: An intramolecular frustrated Lewis pair that consists of a very simple acidic boryl site (BH_2) and a bulky amino group is found to split dihydrogen in a fast and reversible process. Spin-saturation transfer NMR techniques were used to measure the reaction rates and to obtain accurate kinetic parameters.

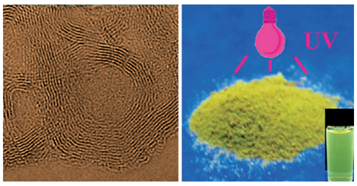
Cycloaddition

Inside Cover



Bridged: The title reaction proceeds via an oxidopyrylium ylide and allows the efficient diastereoselective formation of various synthetically challenging bridged 7-membered ring systems. This direct transformation has a broad substrate scope with high functional-group tolerance and unique *endo* selectivity and gives the bridged ring systems, including the highly strained tricyclic cores of ingenol and cyclocitrinol, in high yields. TMP = 2,2,6,6-tetramethylpiperidine.

Carbon Nanorings

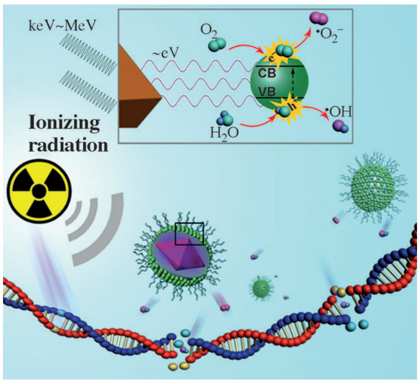


Fluorescent nanomaterials: A one-step hydrothermal method gives intercrossed carbon nanorings (see picture) with relatively pure hydroxy surface states. The hydroxy surface states make it possible to overcome aggregation-induced quenching effects and to emit scarce stable yellow-orange luminescence in both colloidal and solid states.

Glycans

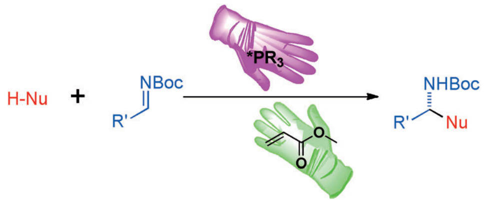
The dynamic single-molecule tracking and super-resolution imaging of N-linked sialic acids and O-linked *N*-acetyl galactosamine (GalNAc) on the membrane of live cells was achieved by using a combination of metabolically labeled glycans and a bioorthogonal copper(I)-catalyzed azide–alkyne cycloaddition. Analysis of the trajectories of the dye-labeled glycans in mammary cancer cells revealed constrained diffusion of both N- and O-linked glycans.

Cancer Therapy



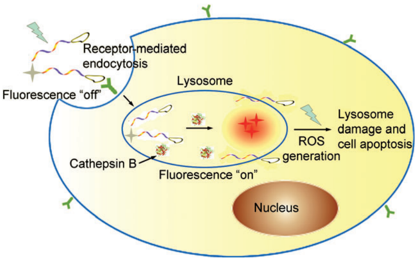
An exemplary marriage: A scintillator and a semiconductor are combined to form an ionizing-radiation-induced photodynamic therapy agent based on a core–shell Ce^{III}-doped $\text{LiYF}_4\text{@SiO}_2\text{@ZnO}$ structure. The downconverted ultraviolet fluorescence from the system under X-ray irradiation enables the generation of electron–hole pairs in ZnO nanoparticles, which gives rise to the formation of biotoxic hydroxyl radicals.

Organocatalysis

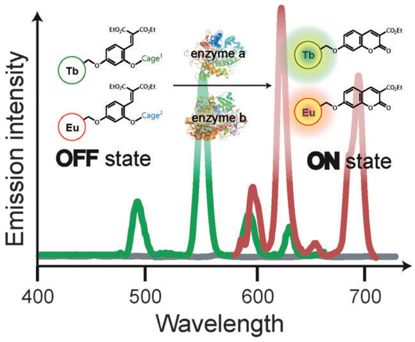


Paired off: A new strategy combines a chiral phosphine with methyl acrylate to form a homogeneous ion pair. This activation mode has been successfully applied to Mannich-type reactions, thus generating a variety of fluorinated amino acid derivatives in high yields and with high *ee* values.

Fluorescent Biological Probes



Target and kill: A dual-targeted enzyme-activatable bioprobe based on a photosensitizer was developed with the characteristics of aggregation-induced emission and aggregation-enhanced phototoxicity (see picture; ROS = reactive oxygen species). The probe enables simultaneous light-up fluorescence imaging and photodynamic ablation of specific cancer cells and shows a high signal-to-noise ratio without the need for a quencher or energy acceptor.

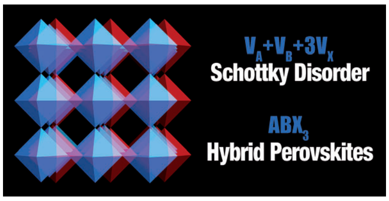


Getting real: The simultaneous, real-time detection of two enzymes or an enzyme and a small molecule by time-resolved luminescence spectroscopy has been demonstrated using lanthanide-based responsive probes. The use of two different lanthanide emitters results in well-separated output signals (see picture), while three-color analyte detection without spectral overlap can be achieved by combination with an organic fluorophore-based probe.

Fluorescent Probes

E. Pershagen, K. E. Borbas* **1787 – 1790**

Multiplex Detection of Enzymatic Activity with Responsive Lanthanide-Based Luminescent Probes

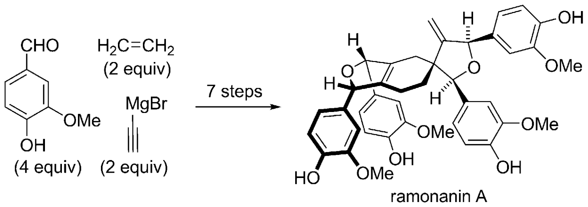


Missing ion action: Schottky defects are found to be a dominant mode of equilibrium stoichiometric disorder in the photovoltaic material $CH_3NH_3PbI_3$. This behavior can explain the previous finding that “the compounds show intense color, but there is no significant conductivity”.

Schottky Disorder

A. Walsh,* D. O. Scanlon,* S. Chen,
X. G. Gong, S.-H. Wei ——— **1791 – 1794**

Self-Regulation Mechanism for Charged Point Defects in Hybrid Halide Perovskites

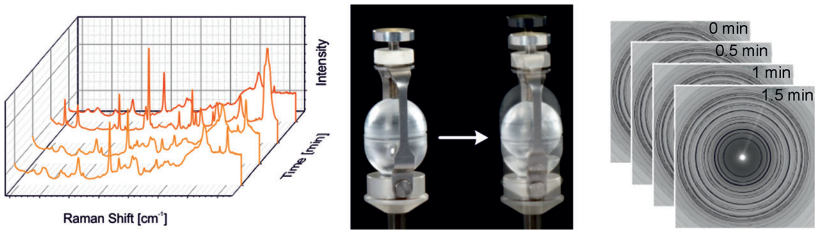


Dimers of dimers: The first total synthesis of the ramonanin family of natural products has been achieved in short order. These natural phenylpropanoid tetramers were assembled in seven steps from the starting materials vanillin, ethylene, and the ethynyl Grignard reagent. Computational studies shed light on a surprisingly facile Diels–Alder dimerization.

Total Synthesis

R. S. Harvey, E. G. Mackay, L. Roger,
M. N. Paddon-Row,* M. S. Sherburn,*
A. L. Lawrence* ——— **1795 – 1798**

Total Synthesis of Ramonanins A–D



Spotlight on mechanochemistry: Reaction mechanisms of milling reactions were investigated in situ and in real time using a combination of X-ray diffraction and Raman spectroscopy (see picture). This method provides a complete picture of the underlying processes, broadening our understanding of milling reactions.

Mechanochemistry

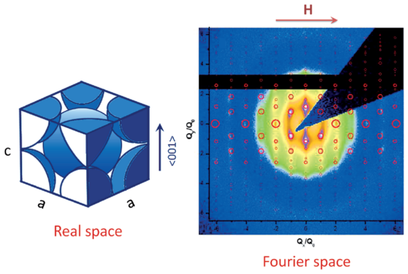
L. Batzdorf, F. Fischer, M. Wilke,
K.-J. Wenzel, F. Emmerling* **1799 – 1802**

Direct In Situ Investigation of Milling Reactions Using Combined X-ray Diffraction and Raman Spectroscopy

Colloidal Crystals

A. Pal, V. Malik, L. He, B. H. Erné, Y. Yin, W. K. Kegel, A. V. Petukhov* **1803 – 1807**

Tuning the Colloidal Crystal Structure of Magnetic Particles by External Field

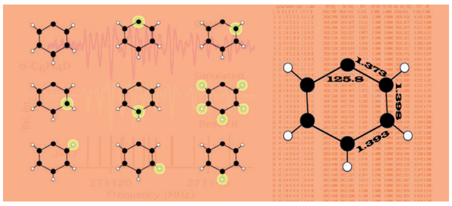


An external magnetic field stimulates core–shell magnetite/silica nanoparticles to self-assemble to a body-centered tetragonal crystalline structure. In the absence of magnetic field, the self-organization is governed by the hard-sphere repulsion between the particles and a combination of electrostatic repulsion and van der Waals attraction, leading to the formation of a random hexagonal close-packed structure.

Molecular Structure

O. Martinez, Jr., K. N. Crabtree, C. A. Gottlieb, J. F. Stanton, M. C. McCarthy* **1808 – 1811**

An Accurate Molecular Structure of Phenyl, the Simplest Aryl Radical

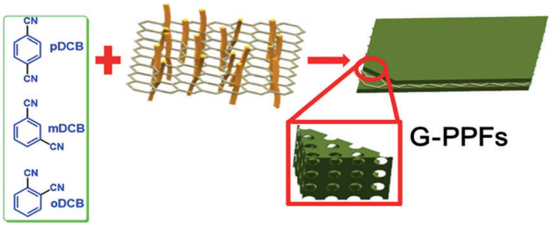


Radical structure: Using a combination of rotational spectroscopy and vibrational corrections calculated theoretically, an extremely accurate molecular structure of the phenyl radical has been determined. Relative to benzene, the phenyl radical has a substantially larger C-C_{ipso}-C bond angle (125.8(3)° vs. 120°), and a shorter distance (2.713(3) Å vs. 2.783(2) Å) between the *ipso* and *para* carbon atoms.

Nanostructures

Y. Su, Y. Liu, P. Liu,* D. Wu, X. Zhuang, F. Zhang, X. Feng* **1812 – 1816**

Compact Coupled Graphene and Porous Polyaryltriazine-Derived Frameworks as High Performance Cathodes for Lithium-Ion Batteries

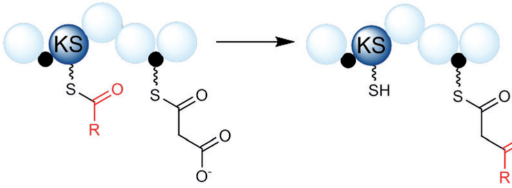


Designer sheets: Designed compact two-dimensional (2D) coupled graphene and porous polyaryltriazine-derived frameworks (G-PPFs) with tailormade porosities are fabricated by employing various dicyanobenzenes in molten $ZnCl_2$ at different temperatures. The 2D porous nanosheets exhibit cycle stability of 395 $mA\,h\,g^{-1}$ at 5 $A\,g^{-1}$ for more than 5100 cycles and a rate capability of 135 $mAh\,g^{-1}$ at a current density of 15 $A\,g^{-1}$.

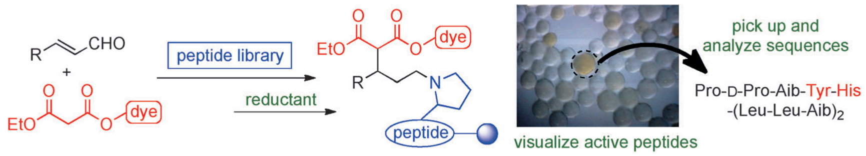
Biosynthesis

M. Jenner, J. P. Afonso, H. R. Bailey, S. Frank, A. Kampa, J. Piel,* N. J. Oldham* **1817 – 1821**

Acyl-Chain Elongation Drives Ketosynthase Substrate Selectivity in *trans*-Acyltransferase Polyketide Synthases



Extension granted: In vitro studies on ketosynthase (KS) domains from *trans*-acyltransferase polyketide synthases were carried out by varying the substrate (R group) and measuring product formation by mass spectrometry. The results revealed substrate selectivity for the chain elongation step that mirrors the predictions based on phylogenetic analysis. Substrate tolerance profiles provide valuable information for the bioengineering of polyketide assembly lines.



Catalytically active peptides were identified from a peptide library by a facile screening method. Reactive amino catalysts can be visualized by anchoring a dye-labeled product. Histidine-containing peptides were found to be efficient catalysts for the enantioselective Michael addition of malonates and enals.

Peptide Catalysis

K. Akagawa, N. Sakai,
K. Kudo* ———— **1822 – 1826**

Histidine-Containing Peptide Catalysts Developed by a Facile Library Screening Method

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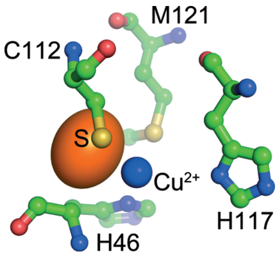

A trilateration approach allows the localization of metal ions within biomolecular structures. Such metal ions are important in the catalysis and folding of biomolecules. The approach utilizes EPR-based long-range distance measurements, and was tested on the Cu^{2+} center of azurin. Factors affecting the precision of the method are discussed.

EPR-Based Trilateration

D. Abdullin, N. Florin, G. Hagelueken,
O. Schiemann* ———— **1827 – 1831**

EPR-Based Approach for the Localization of Paramagnetic Metal Ions in Biomolecules

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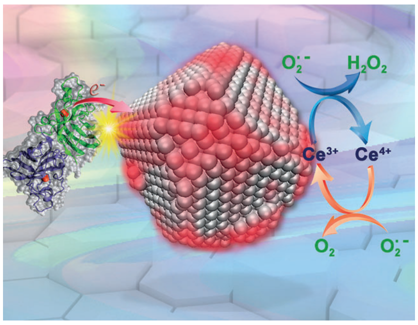

Shaping up: Ceria nanoparticles (nanoceria) with negligible superoxide dismutase mimetic activity have been identified, and they exert antioxidant effects that are much stronger than expected in human bronchial epithelial cells. The underlying mechanism provides a strategy by which nanoceria of custom size, shape, and surface chemistry can acquire remarkable superoxide-scavenging abilities.

Surface Chemistry

Y. Li, X. He,* J.-J. Yin, Y. Ma, P. Zhang, J. Li,
Y. Ding, J. Zhang, Y. Zhao, Z. Chai,
Z. Zhang* ———— **1832 – 1835**

Acquired Superoxide-Scavenging Ability of Ceria Nanoparticles

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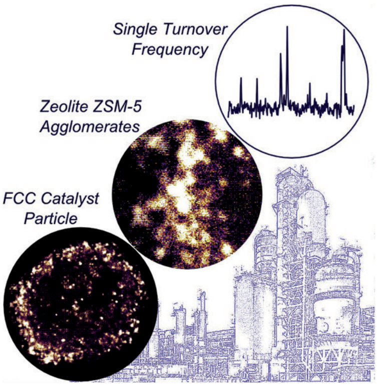


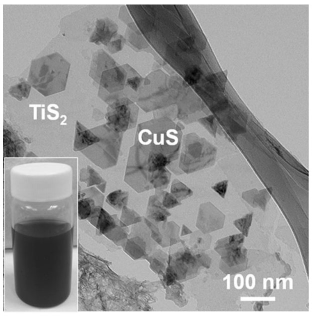
Real-life fluid catalytic cracking (FCC) catalyst particles have been studied with a combination of single-molecule fluorescence nanoscopy and stochastic optical fluctuation imaging methods. Zeolite ZSM-5 aggregates and their reactivity could be mapped with unprecedented spatiotemporal resolution and sensitivity, revealing significant differences in turnover frequencies of the embedded individual zeolite particulates.

Heterogeneous Catalysis

Z. Ristanović, M. M. Kerssens,
A. V. Kubarev, F. C. Hendriks, P. Dedecker,
J. Hofkens, M. B. J. Roeffaers,*
B. M. Weckhuysen* ———— **1836 – 1840**

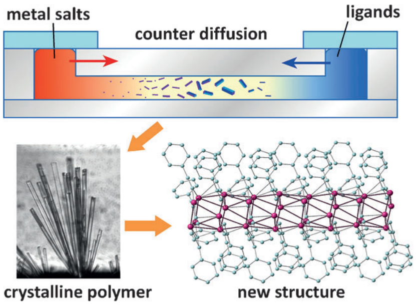
High-Resolution Single-Molecule Fluorescence Imaging of Zeolite Aggregates within Real-Life Fluid Catalytic Cracking Particles

2D Hetero-nanostructures



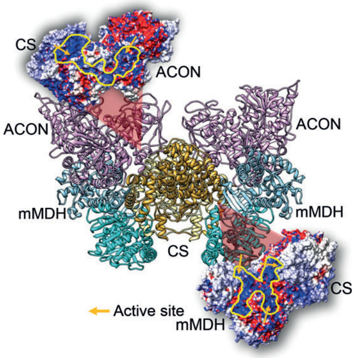
Epitaxial growth of metal sulfide nanoplates, including CuS, ZnS, and Ni_3S_2, on ultrathin TiS_2 nanosheets is achieved by a simple electrochemical approach. Ultrathin triangular/hexagonal CuS nanoplates (50–120 nm) are grown on TiS_2 nanosheets with perfect epitaxial alignment. The 2D CuS–TiS_2 composite is used as anode in a lithium-ion battery, which exhibits high capacity and excellent cycling stability.

Solid-State Structures



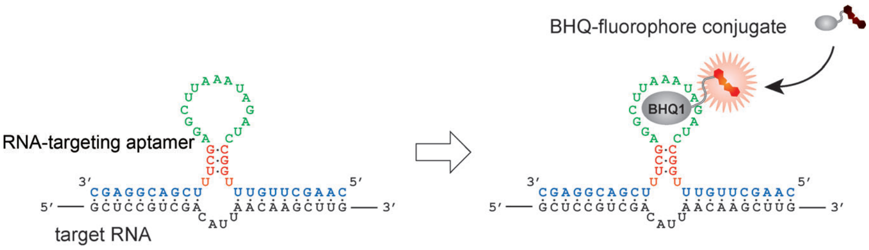
SlowMo flow: A glass microfluidic device was developed for the synthesis and crystallization of organic, inorganic, and polymeric coordination complexes, whose single crystals cannot be obtained using traditional methods. This device is remarkable for its compatibility with organic solvents, the convenience for crystal harvest, the controlled reaction and crystal growth, and the simplicity of fabrication and usage.

Substrate Channeling



Enzymes and channels: Part of the structure of the Krebs cycle metabolon was probed by mass spectrometry. Rational protein docking with cross-link constraints proposed an association of enzymes giving a two-fold symmetric octamer composed of two mMDH dimers and two ACON monomers bound to one CS dimer as the core. The electrostatic channels formed by enzyme association are favorable for direct transport of intermediates between active sites.

Live-Cell Imaging

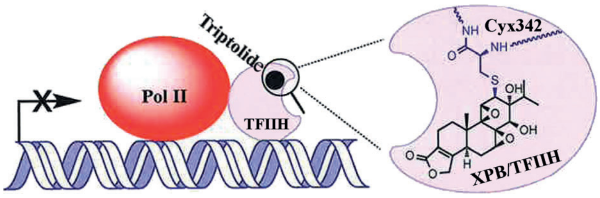


Spatiotemporal imaging of specific non-engineered RNAs in living cells is reported. The used method combined a gene-specific RNA aptamer with a cell-permeable synthetic small molecule, the fluorescence of which is restored only when the RNA aptamer hybridizes with its cognitive target RNA.

Covalent Inhibitors

Q.-L. He, D. V. Titov, J. Li, M. Tan, Z. Ye, Y. Zhao, D. Romo, J. O. Liu* **1859 – 1863**

Covalent Modification of a Cysteine Residue in the XPB Subunit of the General Transcription Factor TFIIH Through Single Epoxide Cleavage of the Transcription Inhibitor Triptolide

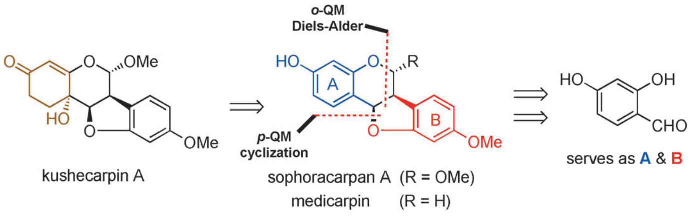


Power trip: Triptolide, a plant secondary metabolite with potent anticancer and immunosuppressive activities, acts by irreversibly inhibiting eukaryotic transcription by RNA polymerase II (Pol II). XPB, a subunit of the general transcription factor TFIIH, was identified as the primary cellular target and the mechanism of action was shown to be the covalent modification of Cys342 of XPB by the 12,13-epoxide group of triptolide.

Total Synthesis

Z. Feng, W. Bai, T. R. R. Pettus* **1864 – 1867**

Unified Total Syntheses of (−)-Medicarpin, (−)-Sophoracarpan A, and (±)-Kushecarpin A with Some Structural Revisions

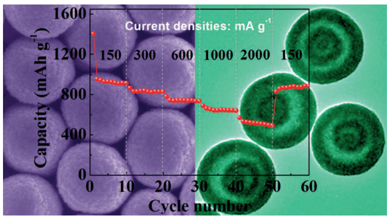


***Ortho-* and *para*-quinone methide** chemistry is used to accomplish the total syntheses of medicarpin, sophoracarpan A, and kushecarpin A from a common intermediate. Additionally, the relative stereochemistry of sophoracarpan A and B have been reassigned. QM = quinone methide.

Mixed Metal Oxides

L. F. Shen, L. Yu, X. Y. Yu, X. G. Zhang, X. W. Lou* **1868 – 1872**

Self-Templated Formation of Uniform $NiCo_2O_4$ Hollow Spheres with Complex Interior Structures for Lithium-Ion Batteries and Supercapacitors

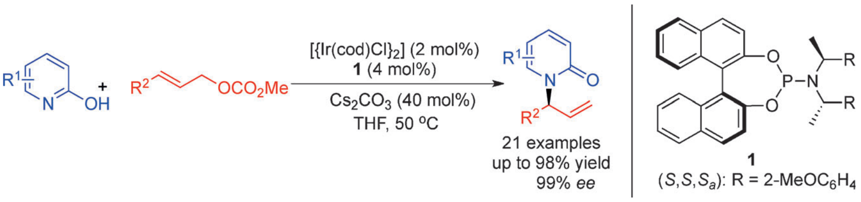


Complex hollow spheres: Metal oxide hollow spheres with complex interior structures were obtained by a strategy involving the solution synthesis of metal glycerate solid spheres and subsequent thermal annealing in air. The image shows $NiCo_2O_4$ core-in-double-shell hollow spheres. Their structural features give rise to an outstanding electrochemical performance as advanced electrode materials for both lithium-ion batteries and supercapacitors.

Asymmetric Catalysis

X. Zhang, Z.-P. Yang, L. Huang, S.-L. You* **1873 – 1876**

Highly Regio- and Enantioselective Synthesis of N-Substituted 2-Pyridones: Iridium-Catalyzed Intermolecular Asymmetric Allylic Amination

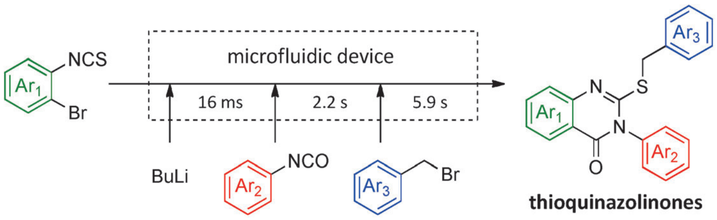


Readily available 2-hydroxypyridines are converted into enantioenriched N-substituted 2-pyridone derivatives by means of a highly efficient method. The title reaction features a good tolerance of functional groups in both the allylic carbonates and 2-hydroxypyridines, thus delivering multifunctionalized heterocyclic products with up to 98 % yield and 99 % *ee*. cod = 1,5-cyclooctadiene.

Microreactor Synthesis

H. Kim, H.-J. Lee,
D.-P. Kim* ______________ **1877 – 1880**

Integrated One-Flow Synthesis of Heterocyclic Thioquinazolinones through Serial Microreactions with Two Organolithium Intermediates

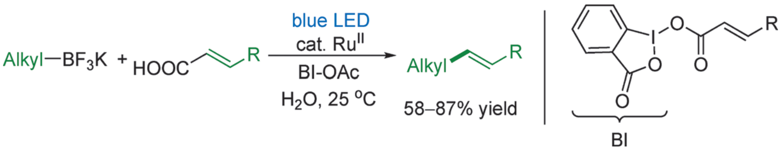


High yield and productivity is achieved for the synthesis of heterocyclic thioquinazolinones by sequential reaction in a one-flow microreactor. This methodology allows control of the residence time of reactive intermediates and significantly speeds up reaction times.

Hypervalent Reagents

H. Huang, K. Jia, Y. Chen* _ **1881 – 1884**

Hypervalent Iodine Reagents Enable Chemoselective Deboronative/ Decarboxylative Alkenylation by Photoredox Catalysis

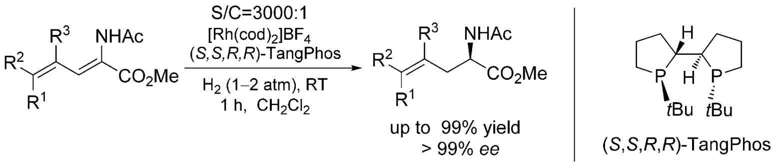


Good visibility: A visible-light-induced chemoselective deboronative/decarboxylative alkenylation is reported. This novel hypervalent-iodine-enabled radical reaction proceeds through a benziodoxole vinyl carboxylic acid intermediate (right). Aryl-and acyl-substituted alkenes containing sensitive functional groups are constructed in good yields. Alkyl = 1’-, 2’-, 3’-alkyl, R = aryl, acyl.

Synthetic Methods

M. Gao, J. Meng, H. Lv,*
X. Zhang* ______________ **1885 – 1887**

Highly Regio- and Enantioselective Synthesis of γ,δ-Unsaturated Amido Esters by Catalytic Hydrogenation of Conjugated Enamides

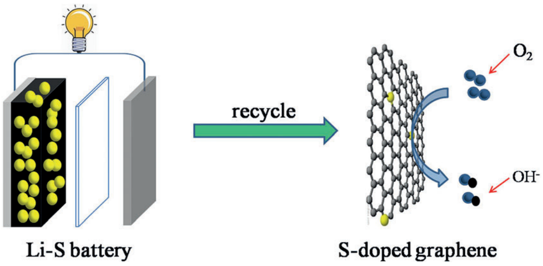


A bit tangy: The Rh/TangPhos-catalyzed asymmetric hydrogenation of α,γ-dienamido esters has been developed and affords γ,δ-unsaturated amido esters with both high regioselectivities and enantioselectivities. This method furnishes products using a high substrate to catalyst ratio (S/C) and with greater than 99 % *ee*. This strategy had been applied in the asymmetric synthesis of key a precursor to Ramipril, an ACE inhibitor. cod = 1,5-cyclooctadiene.

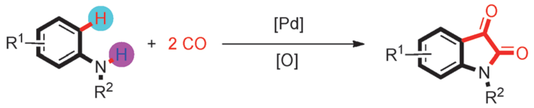
Oxygen Reduction Reaction

Z. Ma, S. Dou, A. Shen, L. Tao, L. Dai,*
S. Wang* ______________ **1888 – 1892**

Sulfur-Doped Graphene Derived from Cycled Lithium–Sulfur Batteries as a Metal-Free Electrocatalyst for the Oxygen Reduction Reaction



Reuse and recycle: By continuous charge/discharge cycling of Li–S batteries containing graphene–sulfur composites, graphene was recycled as sulfur-doped graphene. This material was used as a metal-free electrocatalyst for the oxygen reduction reaction.



Two at once: A novel palladium-catalyzed C–H double carbonylation introduces two adjacent carbonyl groups for the synthesis of isatins from readily available anilines. The reaction proceeds under atmospheric pressure of CO with high regioselectivity and without any additives. Density functional theory investigations indicate that the palladium-catalyzed double carbonylation catalytic cycle is plausible.

Heterocycle Synthesis

W. Li, Z. Duan, X. Zhang, H. Zhang, M. Wang, R. Jiang, H. Zeng, C. Liu, A. Lei* ———— **1893 – 1896**

From Anilines to Isatins: Oxidative Palladium-Catalyzed Double Carbonylation of C–H Bonds

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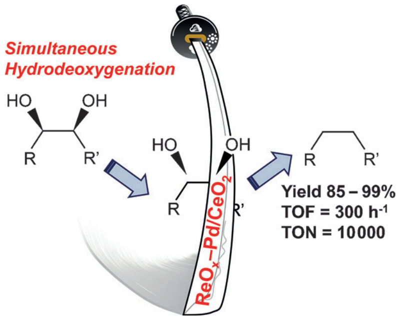

Ultra-fast double cutting: High yields (> 99 %), turnover frequencies (TOF, 300 h^{-1}), turnover numbers (TON, 10 000) are achieved in the simultaneous hydrodeoxygenation of 1,4-anhydroerythritol to tetrahydrofuran over heterogeneous ReO_x–Pd/CeO_2 catalyst. This catalyst can be applied to sugar alcohols; mono-alcohols and diols are obtained in high yields (≥ 85 %).

Hydrodeoxygenation

N. Ota, M. Tamura, Y. Nakagawa,* K. Okumura, K. Tomishige* **1897 – 1900**

Hydrodeoxygenation of Vicinal OH Groups over Heterogeneous Rhenium Catalyst Promoted by Palladium and Ceria Support

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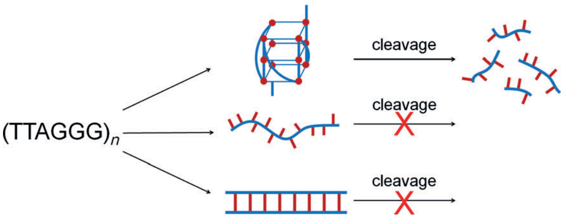

A copper–acridine–ATCUN complex selectively binds and cleaves the G-quadruplex telomere sequence of DNA. The cleavage pathway has been mapped by MALDI-TOF MS experiments. The complex promotes significant inhibition of cancer cell proliferation and telomere shortening, inducing both senescence and apoptosis in the MCF7 cancer cell line.

Catalytic Metallodrug

Z. Yu, M. Han, J. A. Cowan* **1901 – 1905**

Toward the Design of a Catalytic Metallodrug: Selective Cleavage of G-Quadruplex Telomeric DNA by an Anticancer Copper–Acridine–ATCUN Complex

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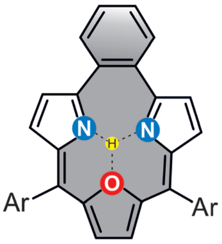
Staying close: Oxatriphyrin(2.1.1) incorporating an *ortho*-phenylene moiety leads to an aromatic compound in which the benzene fragment participates in π delocalization. The proximity of the heteroatoms (N,O,N) results in a strong intramolecular three-centered hydrogen bond. The introduction of boron(III) leads to a complex having a paratropic current.



Aromaticity

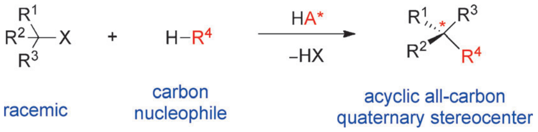
M. Pawlicki,* M. Garbicz, L. Szterenberg, L. Latos-Grażyński* ———— **1906 – 1909**

Oxatriphyrins(2.1.1) Incorporating an *ortho*-Phenylene Motif

Asymmetric Catalysis

W. Zhao, Z. Wang, B. Chu,
J. Sun* ________________ 1910 – 1913

Enantioselective Formation of All-Carbon Quaternary Stereocenters from Indoles and Tertiary Alcohols Bearing A Directing Group

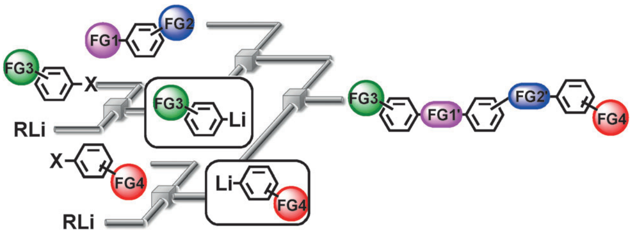


Center on C: An efficient catalytic asymmetric intermolecular C–C bond-formation process generats acyclic all-carbon quaternary stereocenters. The new asymmetric nucleophilic substitution of a range of racemic tertiary alcohols proceeds with excellent bond-formation efficiency and stereocontrol. The enantioenriched indole-containing products and their derivatives are prevalent in natural products and biologically active molecules.

Microreactors

A. Nagaki, K. Imai, S. Ishiuchi,
J.-i. Yoshida* ____________ 1914 – 1918

Reactions of Difunctional Electrophiles with Functionalized Aryllithium Compounds: Remarkable Chemoselectivity by Flash Chemistry

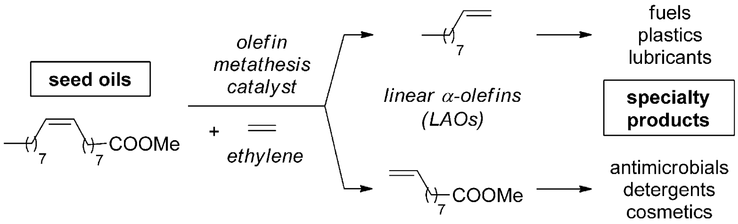


Microreactors: Flash chemistry using flow microreactors enables highly chemoselective reactions of difunctional electrophiles with functionalized aryllithium compounds by virtue of extremely fast micromixing. The approach serves as a powerful method for protecting-group-free synthesis using organolithium compounds.

Renewable Carbon Sources

V. M. Marx, A. H. Sullivan, M. Melaimi,
S. C. Virgil,* B. K. Keitz, D. S. Weinberger,
G. Bertrand,*
R. H. Grubbs* ____________ 1919 – 1923

Cyclic Alkyl Amino Carbene (CAAC) Ruthenium Complexes as Remarkably Active Catalysts for Ethenolysis

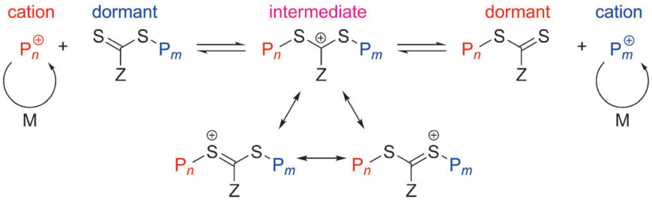


A new series of olefin-metathesis catalysts containing cyclic alkyl amino carbene (CAAC) ligands exhibit unprecedented activity in the ethenolysis of methyl oleate. This work advances the state-of-the-art of the ethenolysis reaction and is expected to find particular use in large-scale industrial applications.

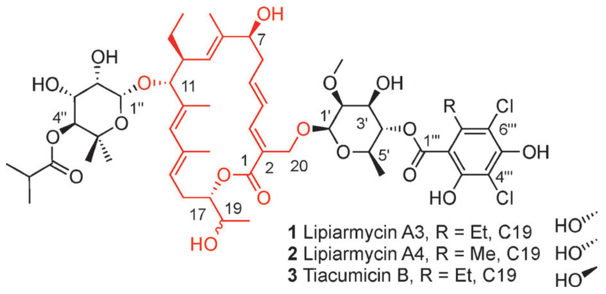
Polymerization

M. Uchiyama, K. Satoh,*
M. Kamigaito* ____________ 1924 – 1928

Cationic RAFT Polymerization Using ppm Concentrations of Organic Acid



Cationic RAFTing: A cationic reversible addition–fragmentation chain-transfer (RAFT) polymerization with thiocarbonylthio compounds proceeds in the presence of a small amount of CF_3SO_3H. Various monomers including vinyl ethers as well as alkoxy- and hydroxystyrene can be used. A transformation from cationic to radical RAFT polymerization enables the synthesis of block copolymers between cationically and radically polymerizable monomers.

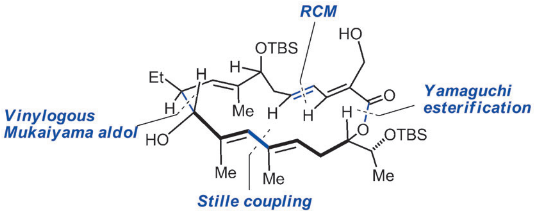


Chain gang: In the synthesis of the title compound, the ene-diene ring-closing metathesis was used for the formation of the 18-membered macrolactone and the stereogenic centers of the molecule were installed by Brown's alkoxyallylboration, allylation, and an Evans aldol reaction, while iterative Horner–Wadsworth–Emmons reactions were used for chain elongation.

Natural Product Synthesis

W. Erb, J.-M. Grassot, D. Linder,
L. Neuville, J. Zhu* ———— 1929 – 1932

Enantioselective Synthesis of Putative Lipiarmycin Aglycon Related to Fidaxomicin/Tiacumicin B

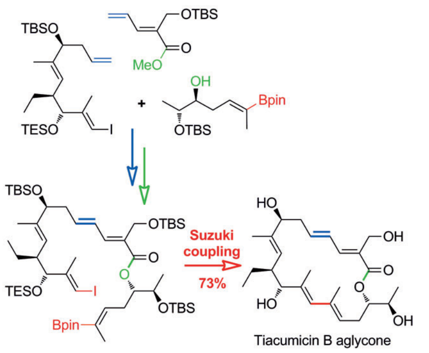


Fidaxomicin fix: The core aglycon of the clinically used antibiotic fidaxomicin was synthesized by using ring-closing metathesis for macrocyclization. This synthetic route is highly convergent and the key steps include a diastereoselective vinylogous Mukaiyama aldol reaction of a novel substrate, Yamaguchi esterification, and a Stille coupling reaction between two sterically hindered intermediates.

Natural Product Synthesis

H. Miyatake-Ondozabal, E. Kaufmann,
K. Gademann* ———— 1933 – 1936

Total Synthesis of the Protected Aglycon of Fidaxomicin (Tiacumicin B, Lipiarmycin A3)



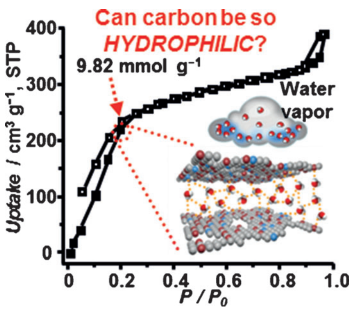
The crucial ring closure in the title total synthesis is effected by an intramolecular Suzuki cross-coupling. Key steps in in the assembly of the linear macrocyclization precursor are a highly selective one-pot Corey–Peterson olefination, which is based on a new thiophenol-mediated *Z*→*E* isomerization of an α,β-unsaturated aldimine, and an ene–diene cross-metathesis reaction.

Natural Product Synthesis

F. Glaus, K.-H. Altmann* —— 1937 – 1940

Total Synthesis of the Tiacumicin B (Lipiarmycin A3/Fidaxomicin) Aglycone

Thirsty materials: A new class of ultra-hydrophilic porous carbon cuboids shows the best performance for atmospheric-water capture among porous carbons to date. It may serve as a model material for research on carbon chemistry, a new material for water capture, and find use in applications requiring highly hydrophilic surfaces, porosity, and stability.



Porous Carbon

G.-P. Hao, G. Mondin, Z. Zheng,
T. Biemelt, S. Klosz, R. Schubel,
A. Eychmüller, S. Kaskel* —— 1941 – 1945

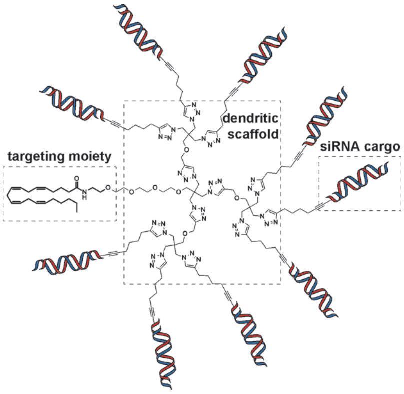
Unusual Ultra-Hydrophilic, Porous Carbon Cuboids for Atmospheric-Water Capture

siRNA Delivery

K. Brunner, J. Harder, T. Halbach, J. Willibald, F. Spada, F. Gnerlich, K. Sparrer, A. Beil, L. Möckl, C. Bräuchle, K.-K. Conzelmann, T. Carell* ________ **1946 – 1949**

Cell-Penetrating and Neurotargeting Dendritic siRNA Nanostructures

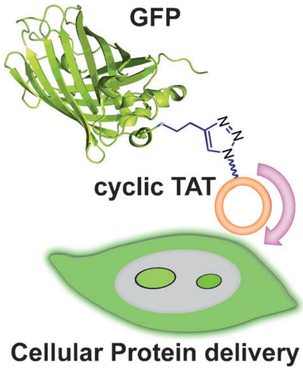
siRNA dendrimers with an anandamide receptor ligand are accessible through a click-chemistry approach, and are taken up even by sensitive neural cells. Silencing of two key proteins of the rabies virus was achieved, allowing the suppression of the viral titer in infected neurons below the detection limit.



Protein Delivery

N. Nischan, H. D. Herce, F. Natale, N. Bohlke, N. Budisa, M. C. Cardoso,* C. P. R. Hackenberger* ____ **1950 – 1953**

Covalent Attachment of Cyclic TAT Peptides to GFP Results in Protein Delivery into Live Cells with Immediate Bioavailability

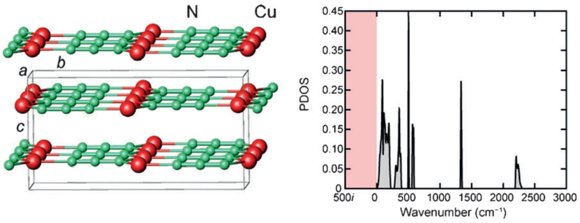


Cycle trip: The conjugation of cyclic cell penetrating peptides (CPPs) to full-length GFP enables direct protein transport into the cell. The cyclic-CPP–GFP conjugates are internalized into live cells with immediate bioavailability, whereas linear CPP analogues are not efficient for GFP transduction. This technology expands the application of cyclic CPPs to the efficient transport of functional full-length proteins into live cells.

Layered Compounds

X. Liu, J. George, S. Maintz, R. Dronskowski* ________ **1954 – 1959**

β-CuN$_3$: The Overlooked Ground-State Polymorph of Copper Azide with Heterographene-Like Layers



Are there others azide from me? A new CuN$_3$ polymorph with a heterographene-like motif was synthesized and characterized. Experimental and theoretical investigations give insight to its thermochemistry and its electronic and vibrational properties. Not only is β-CuN$_3$ identified as the ground-state structure, the compound exhibits negative thermal expansion in the *ab* plane, similar to, but more pronounced, than in graphite.

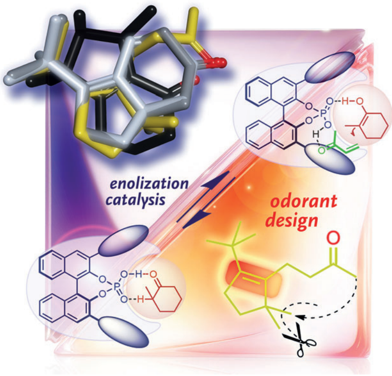
Enol Activation

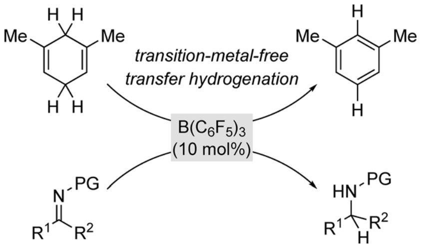
I. Felker, G. Pupo, P. Kraft,* B. List* ________ **1960 – 1964**

Design and Enantioselective Synthesis of Cashmeran Odorants by Using “Enol Catalysis”

Front Cover

Cashmere Wood is the term perfumers use for the typical odor of Cashmeran. Novel representatives of this family were designed and stereoselectively synthesized through enol activation. The key transformation is a chiral phosphoric acid catalyzed Michael addition of enones to α-substituted ketones to afford all-carbon quaternary stereocenters. Olfactory analysis of the target odorants granted insight into the structural requirements for Cashmeran odorants.





Lewis and Brønsted at play: Simple cyclohexa-1,4-dienes with suitably positioned donor substituents in the 1,5-positions serve as reducing agents in the title reaction (see scheme). B(C_6F_5)$_3$ is sufficiently Lewis acidic to abstract a hydride from the bisallylic methylene group at C3 of the cyclohexa-1,4-diene, thereby generating a high-energy Wheland intermediate, in other words, a strong Brønsted acid. The hydride and the proton are then both transferred to the acceptor in a stepwise process.

Transfer Hydrogenation

I. Chatterjee, M. Oestreich* **1965 – 1968**

B(C_6F_5)$_3$-Catalyzed Transfer Hydrogenation of Imines and Related Heteroarenes Using Cyclohexa-1,4-dienes as a Dihydrogen Source

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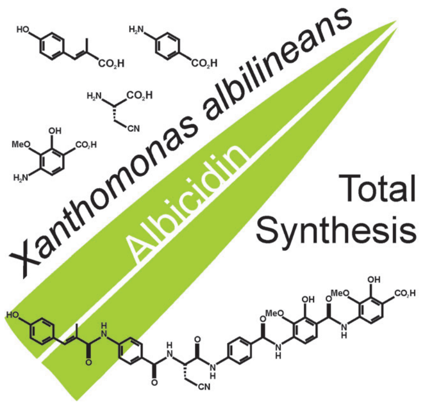

New antibiotics are urgently needed in view of bacterial resistance to established drugs. Albicidin shows activity against various Gram-negative and Gram-positive bacteria, thus making it a promising lead candidate for drug development. The first total synthesis of albicidin was achieved through a convergent synthetic approach that is applicable to the production of derivatives for structure–activity studies.

Natural Product Synthesis

J. Kretz, D. Kerwat, V. Schubert, S. Grätz, A. Pesic, S. Semsary, S. Cociancich, M. Royer, R. D. Süssmuth* **1969 – 1973**

Total Synthesis of Albicidin: A Lead Structure from *Xanthomonas albilineans* for Potent Antibacterial Gyrase Inhibitors

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

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

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

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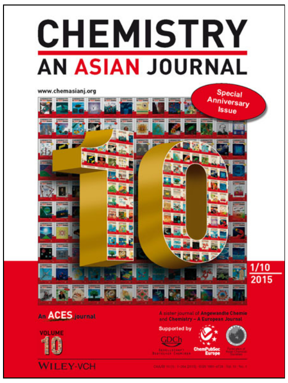
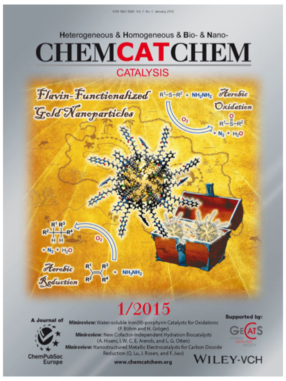


www.chemasianj.org



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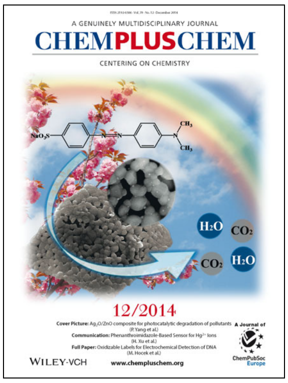
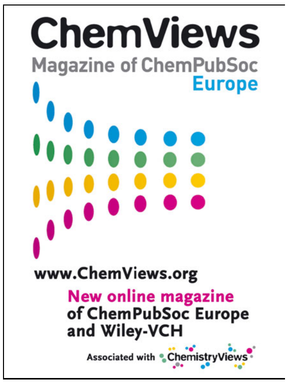


www.chempluschem.org



www.chemviews.org

Angewandte Corrigendum

A Dual-Color Far-Red to Near-Infrared Firefly Luciferin Analogue Designed for Multiparametric Bioluminescence Imaging

A. P. Jathoul, H. Grounds,
J. C. Anderson,*
M. A. Pule* ____________ **13059–13063**

Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201405955

In this Communication, the structure of the penultimate compound in Scheme 1 contains two errors. The OBn substituent should be replaced by an OH group and the CO_2H group should be replaced by a CO_2R group.

Angewandte Corrigendum

On the Molecular Structure and Bonding in a Lithium Bismuth Porphyrin Complex: $LiBi(TPP)_2$

V. Balasanthiran, M. H. Chisholm,*
C. B. Durr ______________ **1594–1597**

Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201308672

The N2–Bi distances found in Figure 3 of this Communication were reported as 2.255(3) Å due to a typographical error. These distances should instead be reported as 2.355(3) Å (see the corrected version of Figure 3 below). This error does not alter the conclusions of the manuscript.

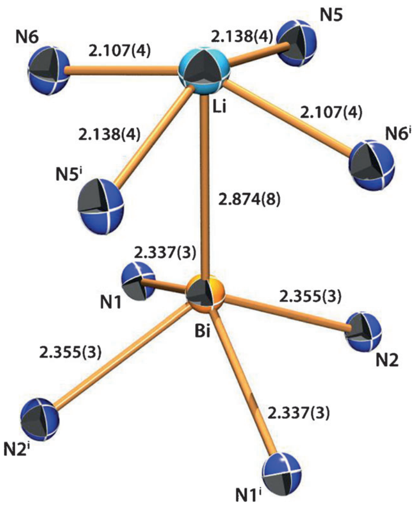


Figure 3. Bond distances in Å surrounding the Bi–Li core.