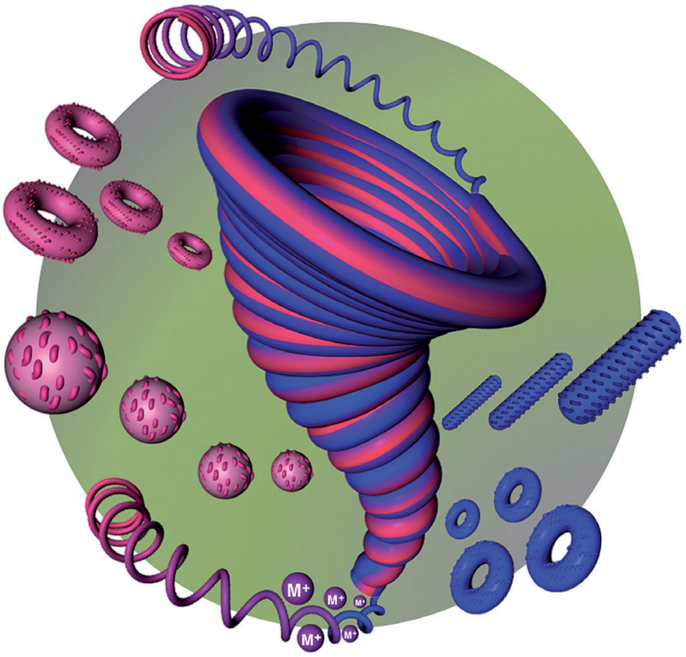
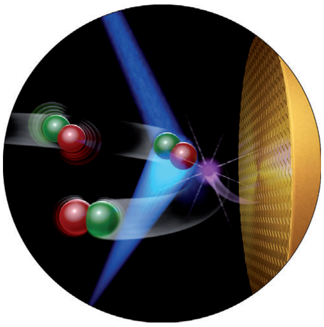
The supramolecular assembly ...

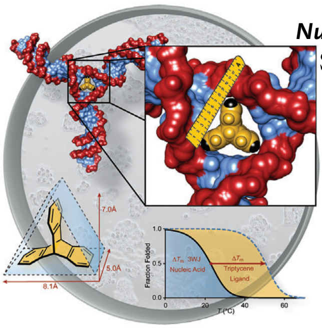


… of helical polymers, namely poly(aryl acetylenes), with monovalent metal cations (Li^+, Na^+, and Ag^+) leads to a number of different macroscopically chiral nanostructures, such as nanospheres, nanotubes, toroids, and gels, with the capacity to encapsulate a variety of organic and inorganic substances. The cover picture illustrates this fruitful "chemical tornado", which is presented by F. Freire, R. Riguera, et al. in their Communication on page 13720.

Surface Chemistry

In their Communication on page 13690 ff., T. Schäfer et al. investigate the transfer of vibrational energy in collisions of an NO molecule with a gold surface. The studies were made possible by the development of new optical pumping and orientation methods.



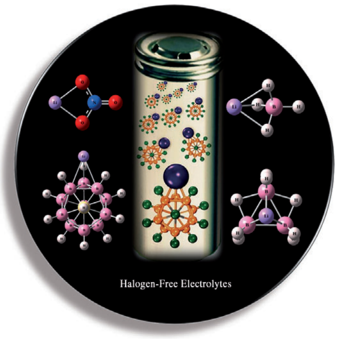


Nucleic Acid Modifications

Structure-specific nucleic acid junction binders based on a triptycene scaffold which significant stabilize DNA and RNA three-way junctions are describe by D. M. Chenoweth and S. A. Barros in their Communication on page 13746 ff.

Electrolytes

P. Jena et al. investigate halogen-free superhalogens and their use as electrolytes in their Communication on p. 13916 ff. $Li(CB_{11}H_{12})$ is shown to be the most promising candidate.



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Editorial

... We should not only honor the history of chemistry by commemorating anniversaries, but also acknowledge it as one of our disciplines. According to Wilhelm von Humboldt, it is only knowledge of the history of chemistry that gives us the best prerequisites for shaping the future of chemistry—from a stronger interdisciplinary and an international perspective ...
Read more in the Editorial by Thomas Geelhaar.

Service

Author Profile

“My biggest inspiration is nature.
My favorite time of day is the evening ...”
This and more about Dongyuan Zhao can be found on page 13648.

News


M. Malacria


M. Ephritikhine


M. Beller


N. Martín


M. Holzinger


S. Sabo-Etienne


B. Nay


F.-X. Felpin


S. Bernard


C. Boissière


A. Ghoufi


B. Le Guennic

Books

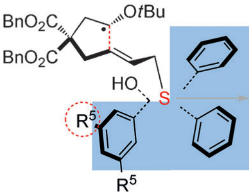
Highlights

Synthetic Methods

H. Subramanian, R. Moorthy,
M. P. Sibi* ______ **13660 – 13662**

Thiyl Radicals: From Simple Radical Additions to Asymmetric Catalysis

Thiyl radicals at play: Thiyls are significant free-radical intermediates both in biology and chemistry. The recent search for new enantioselective methods in radical chemistry has led to the inclusion of these radicals in the toolbox of chiral organocatalysts.

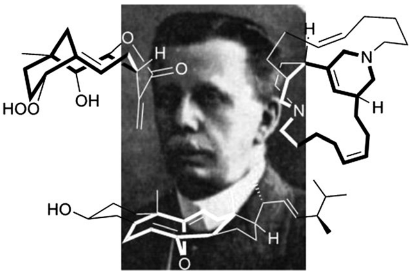


Reviews

Anti-Bredt Olefins

J. Y. W. Mak, R. H. Pouwer,
C. M. Williams* ______ **13664 – 13688**

Natural Products with Anti-Bredt and Bridgehead Double Bonds



Bend it like Bredt: Bredt's rule, developed over a 100 years ago based on simple terpenes, states that the terminus of an olefin cannot exist at the bridgehead position of a bridged bicyclic system. For the first time, complex natural products containing bridgehead olefins and potential anti-Bredt systems are reviewed and evaluated, yet should they be considered anti-Bredt candidates at all?

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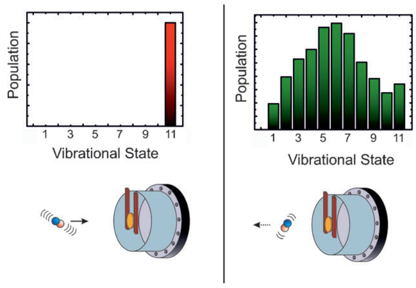
Communications

Surface Chemistry

N. Bartels, B. C. Krüger, D. J. Auerbach,
A. M. Wodtke, T. Schäfer* 13690 – 13694

Controlling an Electron-Transfer Reaction at a Metal Surface by Manipulating Reactant Motion and Orientation

Frontispiece



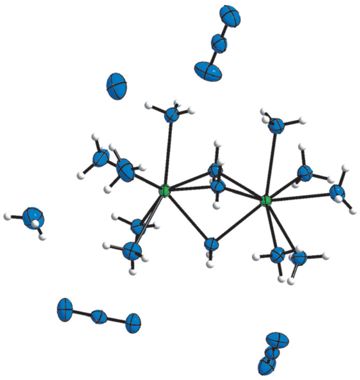
The transfer of vibrational energy in collisions of an NO molecule with a gold surface proceeds by electron transfer. Thanks to new optical pumping and orientation methods, all molecular degrees of freedom important to this process can be controlled. The probability of the electron-transfer reaction is enhanced by increased translational and vibrational energy as well as by proper orientation of the reactant.

Metal Azides

T. G. Müller, F. Karau, W. Schnick,*
F. Kraus* 13695 – 13697

A New Route to Metal Azides

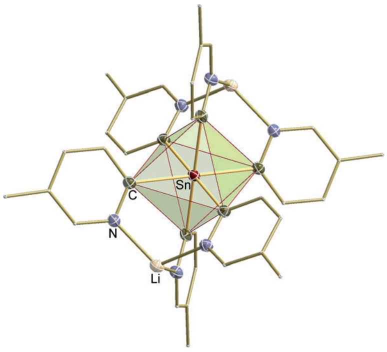
N(ergy) rich: Several metals, such as main-group, transition, and rare-earth metals, react with silver azide in liquid ammonia as the solvent giving the corresponding metal azides. For the first time, $Sn(N_3)_2$ and $Eu(N_3)_2$ as well as their ammonia complexes were synthesized. In addition, ammine complexes of Mn and Ho azide are reported (see structure of $[Ho_2(\mu\text{-}NH_2)_3(NH_3)_{10}](N_3)_3{\cdot}1.25\,NH_3$; green Ho, blue N, white H).



Main-Group Chemistry

I. Schrader, K. Zeckert,*
S. Zahn* 13698 – 13700

Dilithium Hexaorganostannate(IV) Compounds

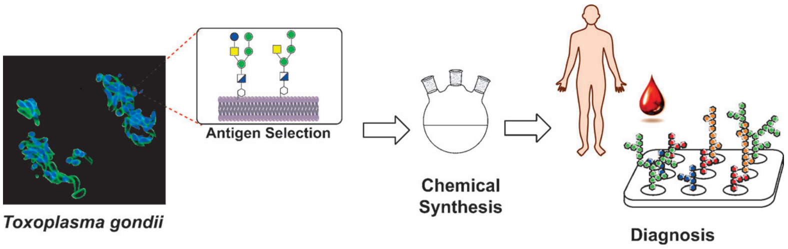


Add in to tin: Tin can readily accommodate more ligands than necessary to complete its Lewis octet. This ability allows it to host six carbon ligands to give the first hexaaryltin(IV) compounds of type $[Sn(2\text{-}py^R)_6]^{2-}$ (see figure). The intramolecular coordination of the Li^+ counterions stabilizes the reactive dianion.

Diagnostic GPI

S. Götze, N. Azzouz, Y.-H. Tsai, U. Groß,
A. Reinhardt, C. Anish, P. H. Seeberger,
D. Varón Silva* 13701 – 13705

Diagnosis of Toxoplasmosis Using a Synthetic Glycosylphosphatidylinositol Glycan

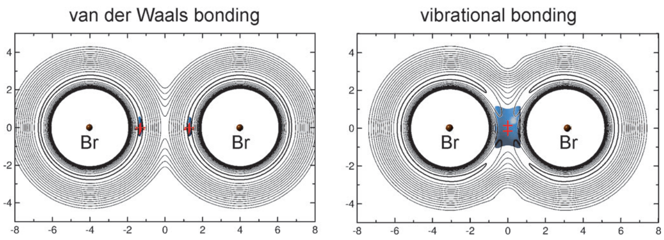


Good news for cat lovers! A glycosylphosphatidylinositol (GPI) glycan resembling an antigen on the parasite *T. gondii* was synthesized and immobilized on a microarray. This setup can be used to diagnose toxoplasmosis. Latent and acute toxoplasmosis can be readily distinguished.

Bonding Theory

D. G. Fleming, J. Manz,* K. Sato,
T. Takayanagi* ____________ **13706 – 13709**

Fundamental Change in the Nature of Chemical Bonding by Isotopic Substitution



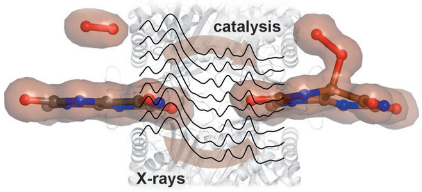
You might think they are the same but in fact they are different. Ab initio calculations reveal a fundamental change from van der Waals bonding of the heavy isotopomers BrHBr, BrDBr, BrTBr, Br^{4}HBr (left) to vibrational bonding of the lightest isotopomer BrMuBr (right).

Enzymatic Mechanisms

S. Bui, D. von Stetten, P. G. Jambrina, T. Prangé, N. Colloc'h, D. de Sanctis, A. Royant, E. Rosta,
R. A. Steiner* ____________ **13710 – 13714**

Direct Evidence for a Peroxide Intermediate and a Reactive Enzyme–Substrate–Dioxygen Configuration in a Cofactor-free Oxidase

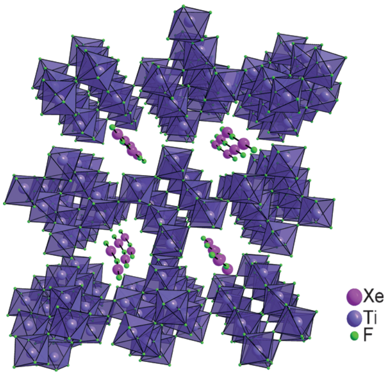
Peroxide intermediate: X-ray crystallography supported by in crystallo Raman spectroscopy and QM/MM methods reveals that the archetypical cofactor-free uricase catalyzes urate degradation via a C5(*S*)-peroxide intermediate. X-rays break the peroxide C5–OO(H) carbon–oxygen bond releasing dioxygen in situ, affording exquisite insight into the reactants' configuration leading to the peroxo intermediate.



Noble-Gas Compounds

K. Radan,* E. Goreshnik,
B. Žemva* ____________ **13715 – 13719**

Xenon(II) Polyfluoridotitanates(IV): Synthesis and Structural Characterization of $[Xe_2F_3]^+$ and $[XeF]^+$ Salts



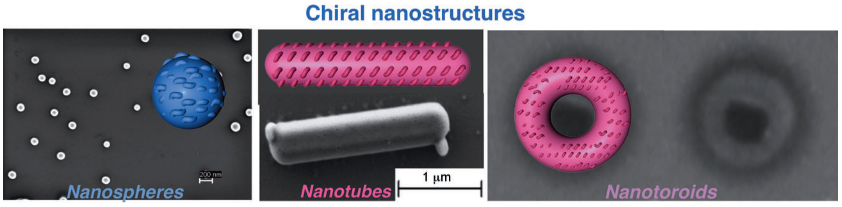
Stronger together: The molecule TiF_4 is unable to efficiently remove fluoride from XeF_2. However, at elevated temperatures, the large polytitanate species formed have an enhanced fluoride affinity, comparable to that of the strongest Lewis acids. Thermal reaction between XeF_2 and TiF_4 afforded colorless crystals the Xe^{II} species $[Xe_2F_3][Ti_8F_{33}]$ (see picture) and $[XeF]_2[Ti_9F_{38}]$ which were isolated and structurally characterized.

Chiral Nanostructures

S. Arias, F. Freire,* E. Quiñoá,
R. Riguera* ____________ **13720 – 13724**

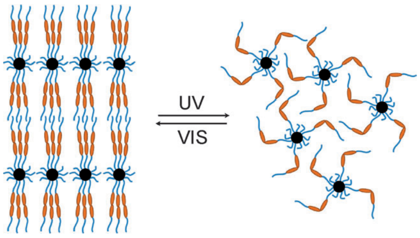
Nanospheres, Nanotubes, Toroids, and Gels with Controlled Macroscopic Chirality

Front Cover



Everything under control: Nanospheres, nanotubes, toroids, and gels are generated by the controlled aggregation of poly(aryl acetylenes) with left- or right-handed helicity with monovalent metal cations (Ag^+, Li^+, and Na^+). The size and helicity of the nanostructures can be tuned, and the nanostructures were used to encapsulate a range of organic and inorganic substances.

Attention!... At ease... Liquid-crystalline (LC) hybrid systems composed of inorganic nanoparticles grafted with photosensitive azo compounds showed reversible melting into an isotropic liquid under UV illumination (see picture). The resulting change in the interparticle distance may enable the design of LC plasmonic materials with light-controlled optical properties.

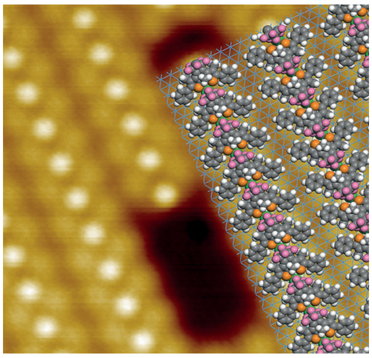


Photosensitive Hybrid Materials

A. Zep, M. M. Wojcik, W. Lewandowski, K. Sitkowska, A. Prominski, J. Mieczkowski, D. Pociecha, E. Gorecka* ______ **13725 – 13728**

Phototunable Liquid-Crystalline Phases Made of Nanoparticles

Only with Na⁺: Diarylethene molecules are arranged into a well-ordered film on Cu(111) through supramolecular assembly with the aid of NaCl co-deposition. Interactions between molecular dipoles and Na^+ cations are the driving force for the superstructure formation.



Supramolecular Chemistry

T. K. Shimizu, J. Jung, H. Imada, Y. Kim* ______ **13729 – 13733**

Supramolecular Assembly through Interactions between Molecular Dipoles and Alkali Metal Ions

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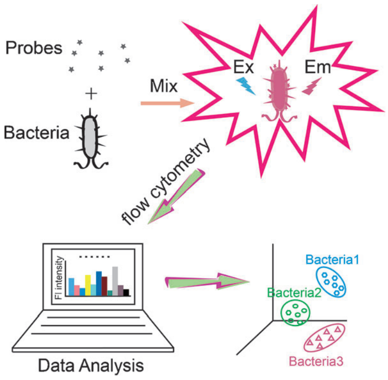
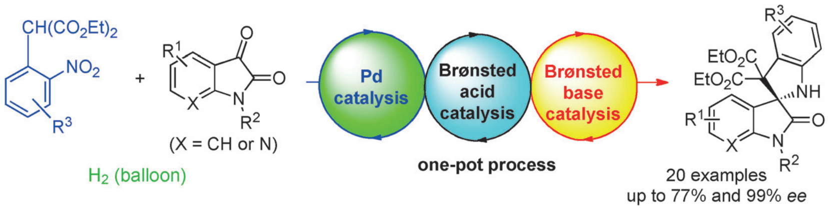


What's this bug? Probes with special fluorescent characteristics are used to fabricate an array (F-array) for bacteria identification with the assistance of statistical methods. Eight kinds of bacteria are discriminated successfully; even normal bacteria and multidrug-resistant bacteria can be distinguished. The method is easy to perform, fast, and effective.

Bacteria Identification

W. Chen, Q. Li, W. Zheng, F. Hu, G. Zhang, Z. Wang,* D. Zhang,* X. Jiang* ______ **13734 – 13739**

Identification of Bacteria in Water by a Fluorescent Array



Oxindole-based spirocyclic indolines were prepared through a one-pot process that involved the hydrogenation of nitroarenes, ketimine formation, and an asymmetric [1,5] electrocyclic reaction. This final step was catalyzed by a bifunctional chiral tertiary amine that also featured a hydrogen bond donor moiety.

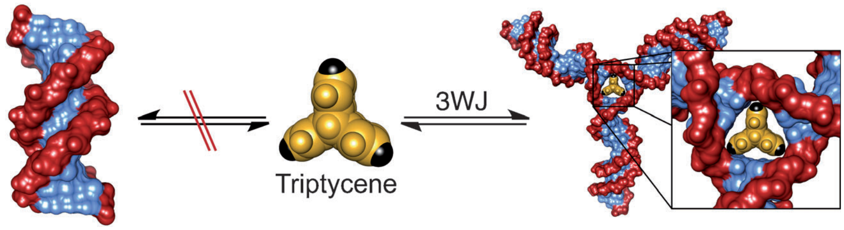
Asymmetric Catalysis

X.-P. Yin, X.-P. Zeng, Y.-L. Liu, F.-M. Liao, J.-S. Yu, F. Zhou, J. Zhou* **13740 – 13745**

Asymmetric Triple Relay Catalysis: Enantioselective Synthesis of Spirocyclic Indolines through a One-Pot Process Featuring an Asymmetric 6π Electrocyclization

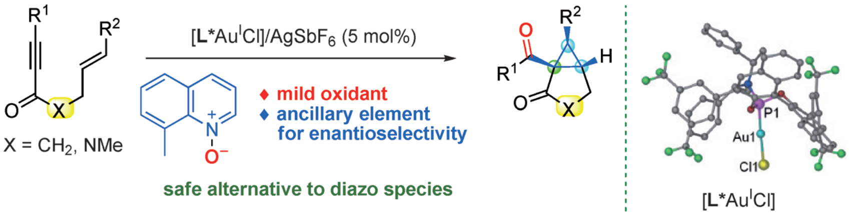
Nucleic Acid Modifications

Inside Back Cover



Structure and function: A new class of structure-specific nucleic acid junction binders based on a triptycene scaffold provides significant stabilization of DNA and RNA three-way junctions (3WJs). Initial biological studies with these junction binders show promising cytotoxicity in cisplatin-resistant human ovarian carcinoma cell lines and positive cellular uptake.

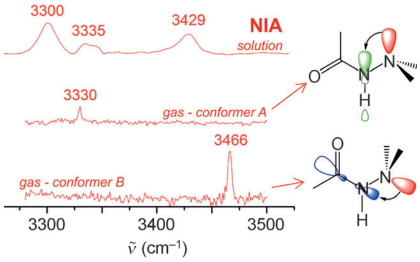
Asymmetric Catalysis



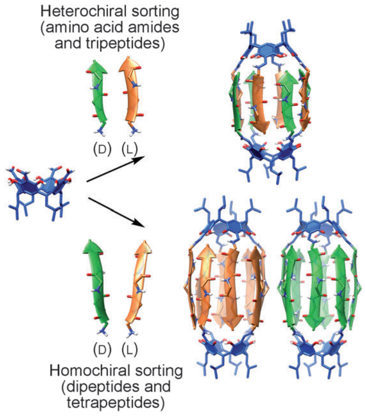
Playing it safe: A highly enantioselective oxidative cyclopropanation of 1,6-enynes with cationic Au$^{\text{I}}$/chiral phosphoramidite catalysts provided convenient access to densely functionalized bicyclo[3.1.0]hexanes with three contiguous quaternary and tertiary stereogenic centers (see scheme; up to 92% yield, e.r. 98:2). Control experiments suggest that the quinoline moiety in the oxidant plays an essential role in the enantioselective cyclopropanation.

Structure Elucidation

Neighborhood watch: IR spectroscopy of hydrazides in the gas phase and in solution has proved to be an efficient probe of the conformation of the neighboring nitrogen atoms. The large hyperconjugation-induced spectral shifts in the NH stretch region enabled a series of hydrazide model molecules to be conformationally characterized.



Supramolecular Chemistry

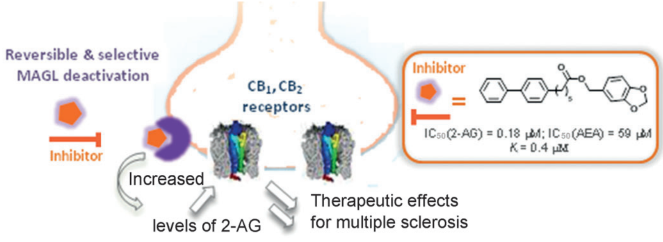


Artificial capsules based on β-barrel binding motifs have been obtained by simultaneous and spontaneous processes involving chiral sorting, selective tautomerization, diastereoselective induction of inherent chirality, and chiral self-assembly. The resulting capsules were selectively formed as heterochiral or homochiral assemblies for peptides with odd and even numbers of residues, respectively.

Enzyme Inhibition

G. Hernández-Torres, M. Cipriano, E. Hedén, S. Björklund, Á. Canales, D. Zian, A. Feliú, M. Mecha, C. Guaza, C. J. Fowler, S. Ortega-Gutiérrez, M. L. López-Rodríguez* __ **13765 – 13770**

A Reversible and Selective Inhibitor of Monoacylglycerol Lipase Ameliorates Multiple Sclerosis



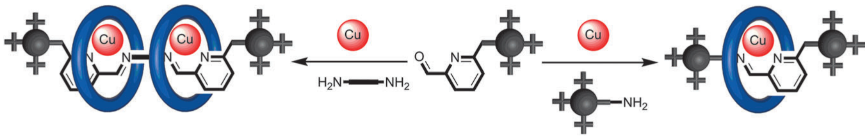
Reversibility is the key: The development of a potent, reversible, selective and in vivo active inhibitor of monoacylglycerol lipase (MAGL), the enzyme responsible for the inactivation of the endocannabinoid 2-arachidonoylglycerol (2-AG), validates, for the first time, the therapeutic potential of MAGL for the treatment of multiple sclerosis.

Inside Cover

Supramolecular Chemistry

C. J. Campbell, D. A. Leigh,* I. J. Vitorica-Yrezabal, S. L. Woltering ________ **13771 – 13774**

A Simple and Highly Effective Ligand System for the Copper(I)-Mediated Assembly of Rotaxanes

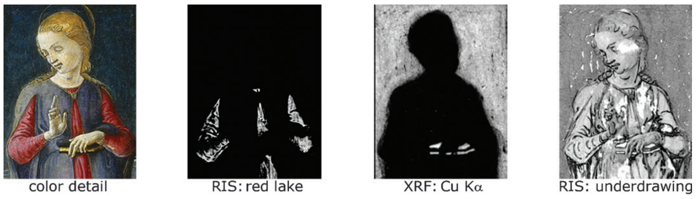


The Cu(I)prit: A [2]rotaxane was produced through the assembly of a picolinaldehyde, an amine, and a bipyridine macrocycle (blue rings) around a Cu^I template by imine bond formation in close-to-quantitative yield. An analogous [3]rotaxane was obtained in excellent yield by replacing the amine with a diamine, thus showing the suitability of the system for the construction of higher order interlocked structures.

Analytical Methods

K. A. Dooley, D. M. Conover, L. D. Glinsman, J. K. Delaney* ________ **13775 – 13779**

Complementary Standoff Chemical Imaging to Map and Identify Artist Materials in an Early Italian Renaissance Panel Painting

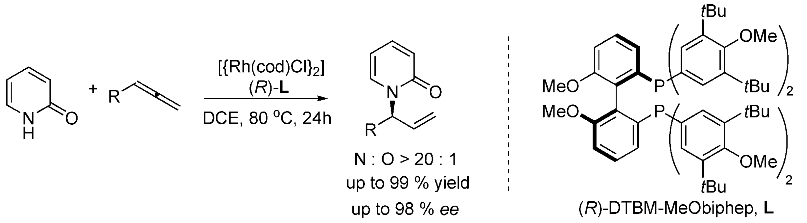


Technical art history: Visible-to-near-infrared reflectance imaging spectroscopy (RIS) and X-ray fluorescence (XRF) imaging spectroscopy were used as complementary chemical imaging methods to provide a robust spatial distribution of pigments. Hyperspectral RIS analysis allowed the isolation of the preparatory drawing from both the overlying original paint of the artist and the inpaint of the conservator.

Pyridone Allylation

C. Li, M. Kähny, B. Breit* **13780 – 13784**

Rhodium-Catalyzed Chemo-, Regio-, and Enantioselective Addition of 2-Pyridones to Terminal Allenes

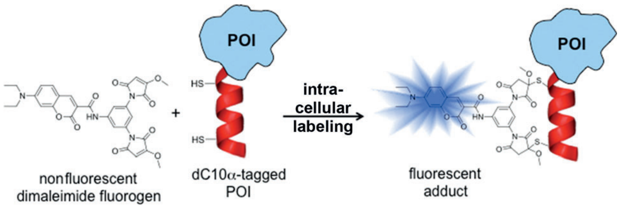


A rhodium-catalyzed chemo-, regio-, and enantioselective addition of 2-pyridones to terminal allenes to give branched N-allyl 2-pyridones is reported. Preliminary mechanistic studies support the hypothesis that the reaction is initiated from the more acidic 2-hydroxypyridine form, and the initial kinetic O-allylation product was finally converted into the thermodynamically more stable N-allyl 2-pyridone.

Bioorthogonal Chemistry

Y. Chen, C. M. Clouthier, K. Tsao,
M. Strmiskova, H. Lachance,
J. W. Keillor* ____________ 13785 – 13788

Coumarin-Based Fluorogenic Probes for No-Wash Protein Labeling

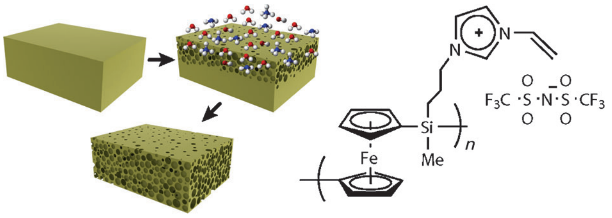


Labeling with FlARe: A coumarin-based dimaleimide labeling agent bearing substituted maleimide groups was prepared. Methoxy substituents were sufficient to attenuate reactivity with glutathione without adversely affecting reactivity with the dithiol target tag (dC10α; red). This kinetic selectivity enables the specific fluorescent labeling of a protein of interest (POI) in living cells through a fluorogenic addition reaction (FlARe).

Stimuli-Responsive Materials

K. Zhang, X. Feng, X. Sui,
M. A. Hempenius,
G. J. Vancso* ____________ 13789 – 13793

Breathing Pores on Command: Redox-Responsive Spongy Membranes from Poly(ferrocenylsilane)s

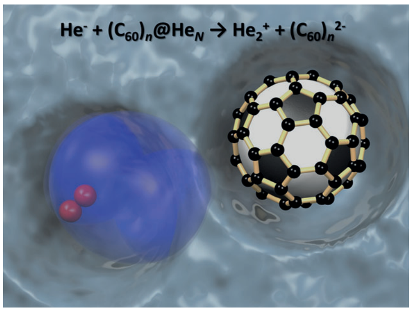


Redox-active porous membranes were synthesized from poly(ferrocenylsilane) PFS-based poly(ionic liquid)s (see picture; pore formation using ammonia/water). Reversible switching between more open and more closed porous structures, induced by oxidation and reduction, was demonstrated.

Electron Transfer

A. Mauracher, M. Daxner, S. E. Huber,
J. Postler, M. Renzler, S. Denifl,
P. Scheier,* A. M. Ellis* __ 13794 – 13797

Formation of Dianions in Helium Nanodroplets

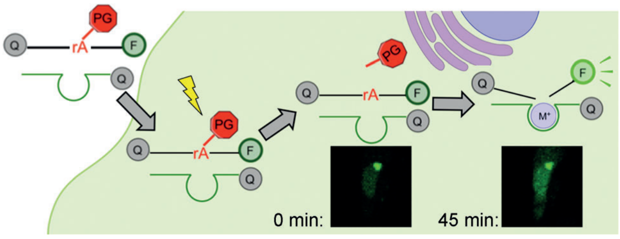


Electron donation from He⁻ to fullerene clusters inside liquid helium nanodroplets has led to the production of doubly charged anions. The evidence suggests that the dianions are made by a concerted two-electron transfer from He⁻, which is a new way of making dianions that may be applicable to other molecules and clusters.

Biosensors

K. Hwang, P. Wu, T. Kim, L. Lei, S. Tian,
Y. Wang, Y. Lu* ____________ 13798 – 13802

Photocaged DNAzymes as a General Method for Sensing Metal Ions in Living Cells

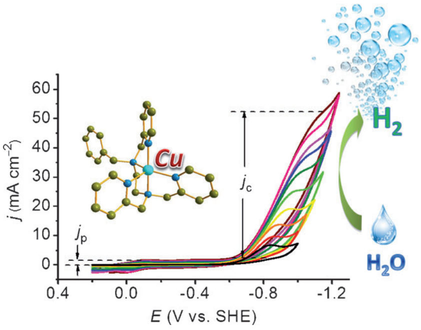


The attachment of a photolabile protecting group (PG) to a DNAzyme allows its delivery into cells, where irradiation with light restores its activity, thus allowing temporal control over the sensing of metal ions. F = fluorophore, Q = quencher.

Hydrogen Production

P. Zhang, M. Wang,* Y. Yang, T. Yao,
L. Sun ——— **13803 – 13807**

A Molecular Copper Catalyst for Electrochemical Water Reduction with a Large Hydrogen-Generation Rate Constant in Aqueous Solution

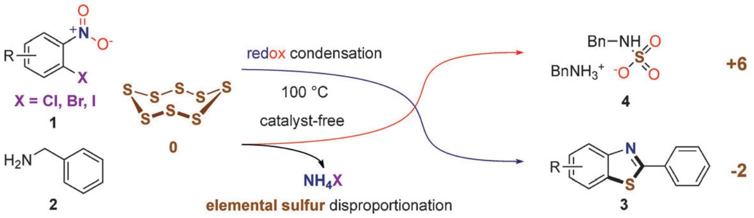


Acidic electrolysis: An ionic copper amine-pyridine complex displayed a hydrogen-generation rate constant (k_{obs}) of over 10000 s^{-1} in pH 2.5 buffer solutions. A turnover frequency of 7000 h^{-1} cm^{-2} and a Faradaic efficiency of 96% were measured in an extended controlled potential electrolysis experiment at −0.90 V versus the standard hydrogen electrode over two hours using a glassy carbon electrode.

Sulfur Disproportionation

T. B. Nguyen,* L. Ermolenko, P. Retailleau,
A. Al-Mourabit* ——— **13808 – 13812**

Elemental Sulfur Disproportionation in the Redox Condensation Reaction between *o*-Halonitrobenzenes and Benzylamines

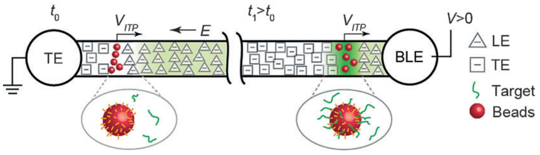


A three-component, metal-free reaction gives 2-arylbenzothiazoles **3** through a redox condensation from *o*-halonitrobenzenes **1** and benzylamines **2**. Elemental sulfur acts as both electron donor and acceptor, generating its lowest and highest oxidation states: S^{2-} in **3** and S^{6+} in sulfamate **4**.

DNA Hybridization Assay

H. Shintaku, J. W. Palko, G. M. Sanders,
J. G. Santiago* ——— **13813 – 13816**

Increasing Hybridization Rate and Sensitivity of Bead-Based Assays Using Isotachophoresis

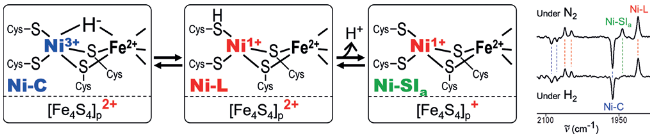


Ten target species per sample can be detected and ssDNA can be quantified with a 100 fM limit of detection by using a bead-based assay with electrokinetic co-focusing of target molecules and beads to speed up reaction. The technique offers similar sensitivity to a well-stirred standard reaction in 60-fold less reaction time. Alternately, for similar reaction time, it offers 5.3-fold higher sensitivity. (B)LE = (buffered) leading electrolyte; TE = trailing electrolyte.

Biocatalysis

H. Tai, K. Nishikawa, M. Suzuki,
Y. Higuchi, S. Hirota* —— **13817 – 13820**

Control of the Transition between Ni-C and Ni-SI$_a$ States by the Redox State of the Proximal Fe–S Cluster in the Catalytic Cycle of [NiFe] Hydrogenase

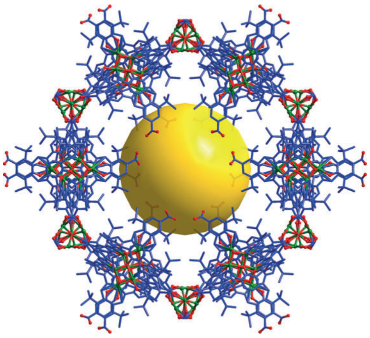


The state of things: The Ni-L state of [NiFe] hydrogenase was found to be an intermediate between the transition of the Ni-C and Ni-SI$_a$ states according to the FT-IR spectra under light irradiation at 138–198 K. This transition occurred when the proximal $[Fe_4S_4]_p^{2+/+}$ cluster was oxidized, but not when it was reduced. These results show that the catalytic cycle of [NiFe] hydrogenase is controlled by the redox state of its $[Fe_4S_4]_p^{2+/+}$ cluster.

Heterogeneous Catalysis

Y. Liu,* X. Xi, C. Ye, T. Gong, Z. Yang,
Y. Cui* ———————— **13821 – 13825**

Chiral Metal–Organic Frameworks Bearing Free Carboxylic Acids for Organocatalyst Encapsulation

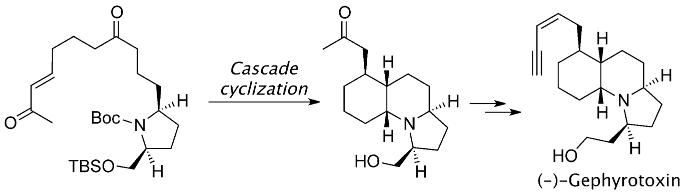


Two chiral carboxylic acid functionalized micro- and mesoporous metal–organic frameworks (MOFs) are constructed. The mesoporous MOF functions as a host for encapsulation of an enantiopure organic amine by acid–base interactions. The organocatalyst-loaded MOF is an efficient and recyclable heterogeneous catalyst for asymmetric direct aldol reactions, with significantly enhanced stereoselectivity relative to the homogeneous organocatalyst.

Total Synthesis

S. Chu, S. Wallace,
M. D. Smith* ———————— **13826 – 13829**

A Cascade Strategy Enables a Total Synthesis of (−)-Gephyrotoxin

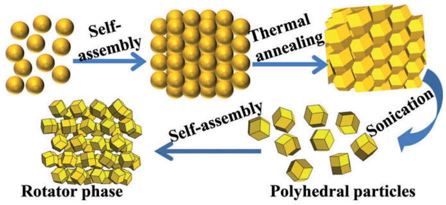


The concise synthesis of (−)-gephyrotoxin from L-pyroglutaminol involves a diastereoselective intramolecular enamine/Michael cascade reaction that forms two rings and two stereocenters and generates a stable tricyclic iminium cation. A hydroxy-directed reduction of this intermediate plays a key role in establishing the required *cis*-configured decahydroquinoline ring system.

Colloids

H. R. Vutukuri,* A. Imhof,
A. van Blaaderen* ———————— **13830 – 13834**

Fabrication of Polyhedral Particles from Spherical Colloids and Their Self-Assembly into Rotator Phases

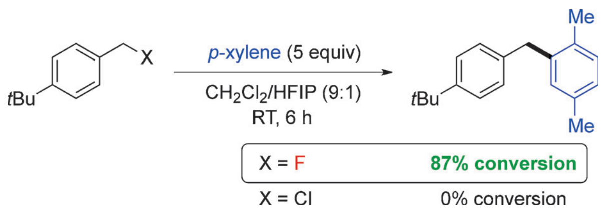


Polyhedral particles: Micrometer-sized polymeric polyhedral particles can be fabricated starting from spheres. The final shape of the particles only depends on the initial three-dimensional assembled structure of the spherical particles. Charged rhombic dodecahedron particles were further used for the formation of three-dimensional rotator phases.

Benzylation

P. A. Champagne, Y. Benhassine,
J. Desroches,
J.-F. Paquin* ———————— **13835 – 13839**

Friedel–Crafts Reaction of Benzyl Fluorides: Selective Activation of C−F Bonds as Enabled by Hydrogen Bonding

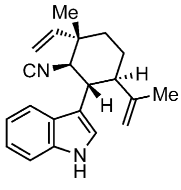


Be selective! A Friedel–Crafts benzylation of arenes with benzyl fluorides (see example; HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol) is proposed to proceed by a mechanism involving activation of the C−F bond through hydrogen bonding. This mode of activation enables the selective reaction of benzylic C−F bonds in the presence of other benzylic leaving groups.

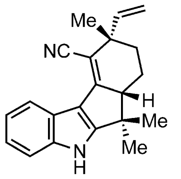
Natural Product Synthesis

Z. Lu, M. Yang, P. Chen, X. Xiong, A. Li* ______ 13840 – 13844

Total Synthesis of Hapalindole-Type Natural Products



12-*epi*-hapalindole Q isonitrile



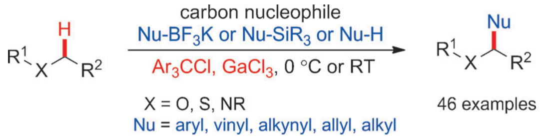
12-*epi*-fischerindole I nitrile

A Prins-type oxidative cyclization reaction was used to accomplish the total syntheses of a number of structurally diverse natural products of the hapalindole family, including hapalindoles Q and H. This strategically novel and flexible approach may facilitate biological studies of these natural products and their analogues.

C—H functionalization

M. Wan, Z. Meng, H. Lou, L. Liu* ______ 13845 – 13849

Practical and Highly Selective C—H Functionalization of Structurally Diverse Ethers

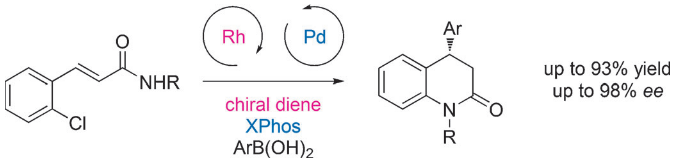


A practical trityl ion mediated C—H functionalization of ethers proceeds at ambient temperature with high chemoselectivity and good functional-group tolerance. The method displays excellent regio- and diastereoselectivities for unsymmetric ethers, thus stereoselectively yielding highly functionalized *trans*-disubstituted tetrahydrofuran, tetrahydropyran, dihydropyran, and isochroman moieties.

Multicatalytic Reactions

L. Zhang, Z. Qureshi, L. Sonaglia, M. Lautens* ______ 13850 – 13853

Sequential Rhodium/Palladium Catalysis: Enantioselective Formation of Dihydroquinolinones in the Presence of Achiral and Chiral Ligands

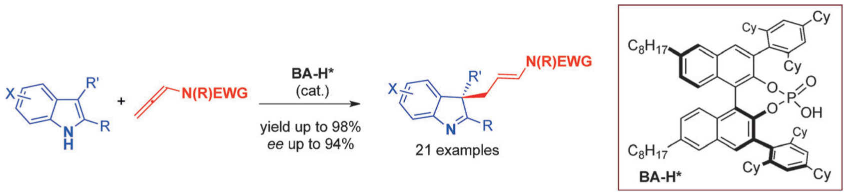


Compatible combinations of achiral and chiral ligands and sequential rhodium/palladium catalysis enabled highly enantioselective domino reactions. The difference in rates of catalysis and minimal ligand interference confer control in the domino sequence. The sequential 1,4-conjugate arylation and C—N cross-coupling provide access to enantioenriched dihydroquinolinone building blocks.

Organocatalysis

C. Romano, M. Jia, M. Monari, E. Manoni, M. Bandini* ______ 13854 – 13857

Metal-Free Enantioselective Electrophilic Activation of Allenamides: Stereoselective Dearomatization of Indoles



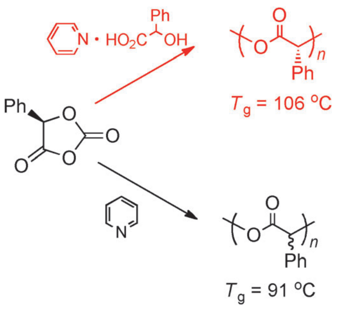
Breaking the aromaticity: The enantioselective dearomatization of indoles with allenamides is achieved through Brønsted acid catalysis. A range of 3,3-disubstituted indolines as well as indolenines is synthesized in a highly chemo-, regio-, and stereoselective manner.

Polymerization

A. Buchard, D. R. Carbery,* M. G. Davidson,* P. K. Ivanova, B. J. Jeffery, G. I. Kociok-Köhn, J. P. Lowe ______ **13858 – 13861**

Preparation of Stereoregular Isotactic Poly(mandelic acid) through Organocatalytic Ring-Opening Polymerization of a Cyclic *O*-Carboxyanhydride

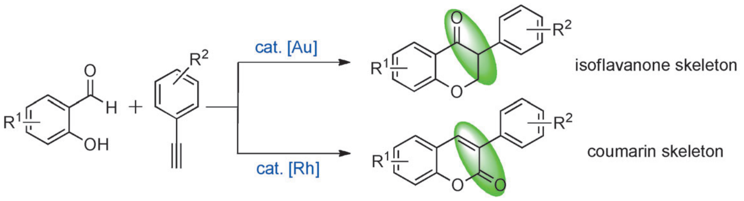
Controlling tactic(s): The use of pyridine alone as the organocatalyst of the ring-opening polymerization (ROP) of a cyclic *O*-carboxyanhydride resulted in atactic poly(mandelic acid) (PMA), however, a well-defined pyridine/mandelic acid adduct enabled excellent control over the ROP, providing highly isotactic chiral PMA with an enhanced heat resistance. T_g = glass-transition temperature.



Rhodium Catalysis

H. Y. Zeng, C.-J. Li* ______ **13862 – 13865**

A Complete Switch of the Directional Selectivity in the Annulation of 2-Hydroxybenzaldehydes with Alkynes

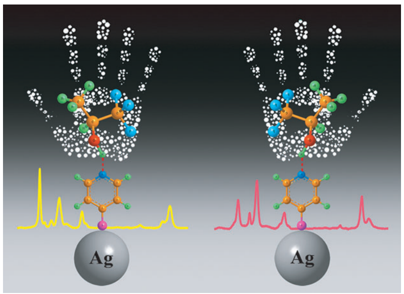


Rodeo rhodium: Different natural product skeletons can be obtained from the same simple starting materials by using different catalytic systems. The gold-catalyzed annulation of terminal alkynes and salicylaldehydes yielded isoflavanones, whereas the rhodium-catalyzed version led to coumarin skeletons.

Raman Spectroscopy

Y. Wang, Z. Yu, W. Ji, Y. Tanaka, H. Sui, B. Zhao,* Y. Ozaki* ______ **13866 – 13870**

Enantioselective Discrimination of Alcohols by Hydrogen Bonding: A SERS Study

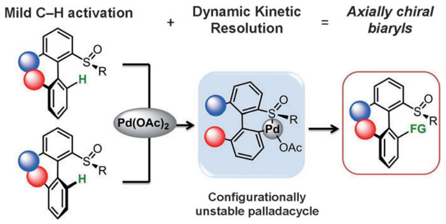


Efficient and generic enantioselective discrimination of various chiral alcohols is achieved by surfaced-enhanced Raman scattering (SERS) spectroscopy. This approach is label-free, does not employ any chiral reagents, and may lead to the development of novel enantiosensing strategies.

C–H Activation

C. K. Hazra, Q. Dherbassy, J. Wencel-Delord,* F. Colobert* ______ **13871 – 13875**

Synthesis of Axially Chiral Biaryls through Sulfoxide-Directed Asymmetric Mild C–H Activation and Dynamic Kinetic Resolution

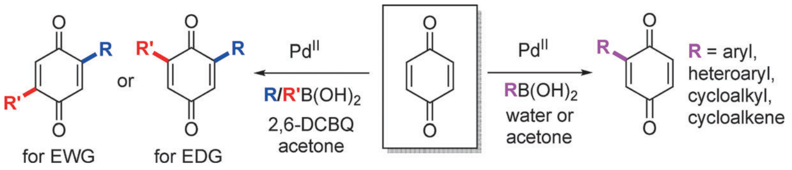


Pd makes it rotate: A C–H activation/dynamic kinetic resolution method allows access to axially chiral biaryls. The isomerization step is believed to occur via a palladacyclic intermediate. Chiral induction is achieved using the sulfoxide motif as both “traceless” directing group and chiral source.

Synthetic Methods

S. E. Walker, J. A. Jordan-Hore,
D. G. Johnson, S. A. Macgregor,*
A.-L. Lee* ―――― 13876 – 13879

Palladium-Catalyzed Direct C–H Functionalization of Benzoquinone



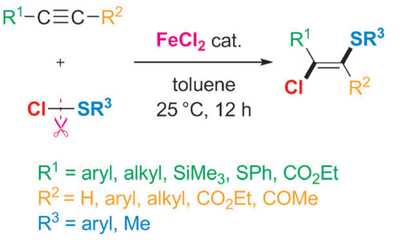
Direct C–H functionalization of benzoquinone in water or acetone is now possible with Pd catalysis. The reaction can be controlled to afford either the mono- or the disubstituted product, and the difunctionalization includes the installation of two different groups in a one-pot procedure. 2,6-DCBQ = 2,6-dichloro-1,4-benzoquinone, EDG = electron-donating group, EWG = electron-withdrawing group.

Iron Catalysis

M. Iwasaki, T. Fujii, K. Nakajima,
Y. Nishihara* ―――― 13880 – 13884

Iron-Induced Regio- and Stereoselective Addition of Sulfenyl Chlorides to Alkynes by a Radical Pathway

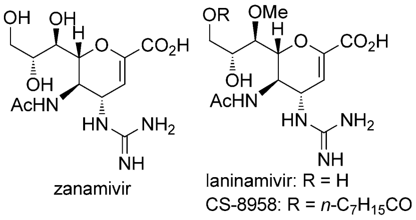
Radical action: Regio- and stereoselective chlorothiolation of alkynes is achieved with an inexpensive and abundant iron catalyst. The reaction simultaneously installs chloro and sulfenyl moieties on terminal and internal alkynes, providing synthetically useful tri- and tetrasubstituted alkenes with excellent selectivity by a radical pathway. The utility of the reaction is shown by transformations of the adducts using cross-coupling reactions.



Asymmetric Synthesis

J. Tian, J. Zhong, Y. Li,
D. Ma* ―――― 13885 – 13888

Organocatalytic and Scalable Synthesis of the Anti-Influenza Drugs Zanamivir, Laninamivir, and CS-8958

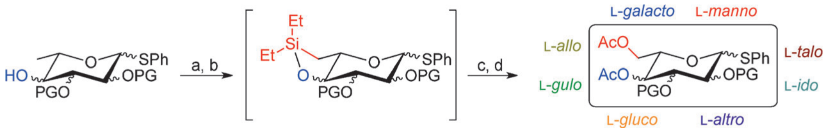


A strategy to combat the flu: The anti-influenza drugs zanamivir and laninamivir (see structures) were synthesized in only 13 steps from inexpensive D-arabo-ascorbic acid by the use of an organocatalytic Michael addition and a metal-catalyzed *anti*-selective Henry reaction as key transformations. This cost-effective, straightforward, and efficient approach enabled the synthesis of more than 3.5 g of zanamivir.

L-Hexoses through C–H Activation

T. G. Frihed, C. M. Pedersen,*
M. Bols ―――― 13889 – 13893

Synthesis of All Eight L-Glycopyranosyl Donors Using C–H Activation

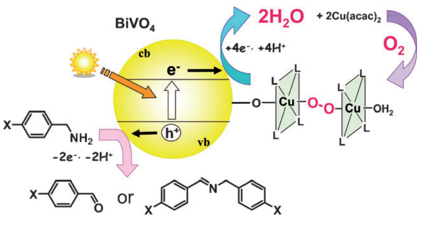


A one-pot four-step procedure was developed for the synthesis of all eight L-glycopyranosyl donors from the corresponding 6-deoxy thioglycosides. Ir-catalyzed silylation (a) and C–H activation (b), followed by a Fleming–Tamao oxidation (c) and acetylation (d) led to highly functionalized thioglycosides.

Multi-Electron Oxygen Reduction

S.-i. Naya, T. Niwa, R. Negishi,
H. Kobayashi,* H. Tada* **13894 – 13897**

Multi-Electron Oxygen Reduction by a Hybrid Visible-Light-Photocatalyst Consisting of Metal-Oxide Semiconductor and Self-Assembled Biomimetic Complex

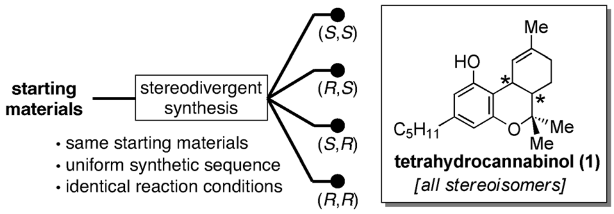


Light-driven oxidation of benzylamines to aldehydes and imines with air at 25 °C with selectivities of more than 99% and without sacrificial reagents is achieved by a biomimetic hybrid photocatalyst. The catalyst is obtained by chemisorption of Cu(acac)$_2$ onto BiVO$_4$ to form an O$_2$-bridged binuclear complex. The multi-electron reduction of O$_2$ is induced by visible-light irradiation. vb = valence band, cb = conducting band.

Natural Product Synthesis

M. A. Schafroth, G. Zuccarello,
S. Krautwald, D. Sarlah,
E. M. Carreira* **13898 – 13901**

Stereodivergent Total Synthesis of Δ^9-Tetrahydrocannabinols

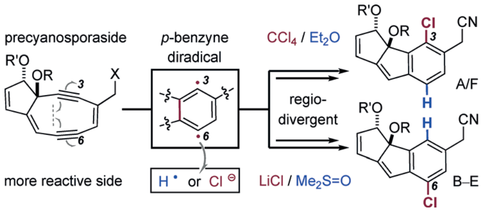


No stereoisomer left behind: A concise synthesis of tetrahydrocannabinol (THC) is described that provides rapid and controlled access to any stereoisomer of the product, including the naturally occurring stereoisomers Δ^9-*trans*-THC and Δ^9-*cis*-THC. By application of stereodivergent dual catalysis to the same set of starting materials, all four isomers of THC were obtained in five steps using a uniform synthetic sequence and identical reaction conditions.

Bioinspired Synthesis

K. Yamada, M. J. Lear,* T. Yamaguchi,
S. Yamashita, I. D. Gridnev, Y. Hayashi,
M. Hirama* **13902 – 13906**

Biomimetic Total Synthesis of Cyanosporaside Aglycons from a Single Enediyne Precursor through Site-Selective *p*-Benzyne Hydrochlorination

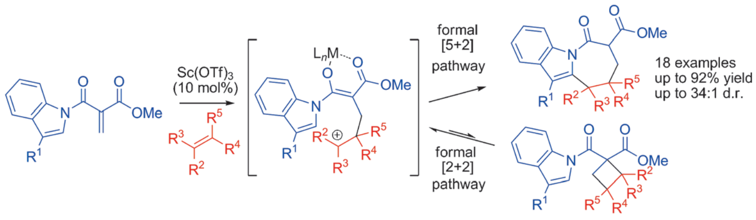


(Di)radical behavior: A close synthetic mimic of an elusive bicyclic nine-membered enediyne is shown to spontaneously rearrange into a transient *p*-benzyne diradical. This diradical reacts both radically (by H abstraction) and ionically (by Cl addition) at the same sterically exposed C6 site, thus revealing its central role in the biosynthesis of all monochlorinated cyanosporasides A to F.

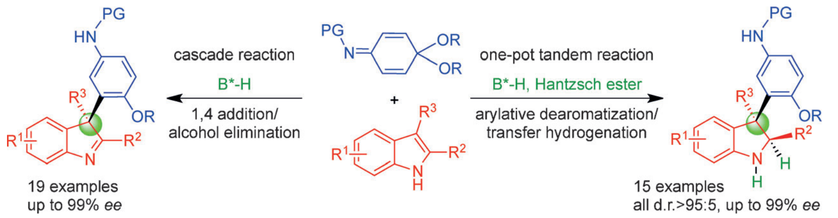
Azepines

R. Shenje, M. C. Martin,
S. France* **13907 – 13911**

A Catalytic Diastereoselective Formal [5+2] Cycloaddition Approach to Azepino[1,2-*a*]indoles: Putative Donor–Acceptor Cyclobutanes as Reactive Intermediates



The diastereoselective synthesis of azepino[1,2-*a*]indoles is enabled by a formal [5+2] cycloaddition approach. The reaction presumably proceeds through a Lewis acid catalyzed formal [2+2] cycloaddition of an alkene with an *N*-indolyl alkylidene β-amide ester to form a donor–acceptor cyclobutane intermediate, which subsequently undergoes an intramolecular ring-opening cyclization.



Less aromatic: The title reaction between indoles and quinone imine ketals was achieved by the two tandem approaches shown in the scheme. In both cases, enantiomerically pure indole derivatives bearing an all-carbon quaternary stereogenic center were generated in high yields and excellent stereoselectivities.

Dearomatization

Y.-C. Zhang, J.-J. Zhao, F. Jiang, S.-B. Sun, F. Shi* **13912 – 13915**

Organocatalytic Asymmetric Arylative Dearomatization of 2,3-Disubstituted Indoles Enabled by Tandem Reactions

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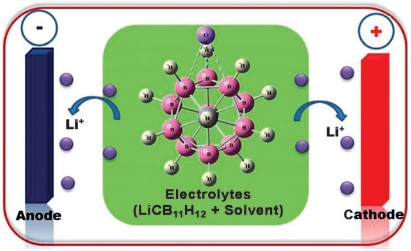


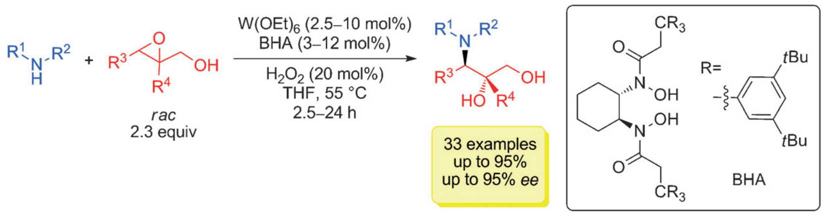
Halogen-free electrolytes: An in-depth study based on first-principles calculations shows that the anions of commercially available electrolytes for Li-ion batteries are all superhalogens. With this knowledge, several halogen-free superhalogen electrolytes with comparable characteristics are identified.

Electrolytes for Li-Ion Batteries

S. Giri, S. Behera, P. Jena* **13916 – 13919**

Superhalogens as Building Blocks of Halogen-Free Electrolytes in Lithium-Ion Batteries

Back Cover



The first enantioselective aminolysis of 2,3-epoxy alcohols involves the use of a tungsten catalyst with a bis(hydroxamic acid) (BHA) ligand. A sequential reaction process combining epoxidation and ring opening (by kinetic resolution) provides a new method for the preparation of virtually enantiopure amino alcohols.

Kinetic Resolution

C. Wang, H. Yamamoto* **13920 – 13923**

Tungsten-Catalyzed Regio- and Enantioselective Aminolysis of *trans*-2,3-Epoxy Alcohols: An Entry to Virtually Enantiopure Amino Alcohols

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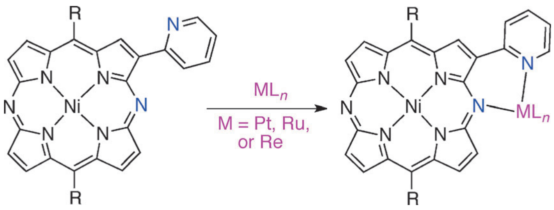


Porphyrin coordination: A 3-pyridyl-5,15-diazaporphyrin Ni^{II} complex acts as a bidentate metalloligand forming stable metal complexes with Pt^{II}, Ru^{II}, and Rh^{I} centers (see picture). Single-crystal X-ray analysis confirms the formation of dative bonds between the *meso*-nitrogen atoms and the metal ions.

Azaporphyrin Ligands

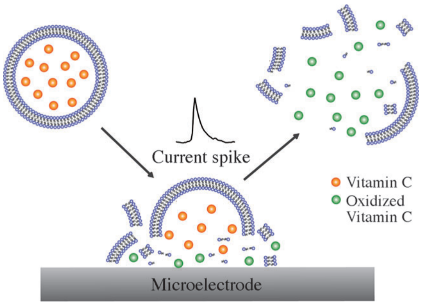
A. Yamaji, J.-Y. Shin, Y. Miyake, H. Shinokubo* **13924 – 13927**

A 3-Pyridyl-5,15-Diazaporphyrin Nickel(II) Complex as a Bidentate Metalloligand for Transition Metals

Electrochemistry

W. Cheng,
R. G. Compton* ________ **13928 – 13930**

Investigation of Single-Drug-Encapsulating Liposomes using the Nano-Impact Method



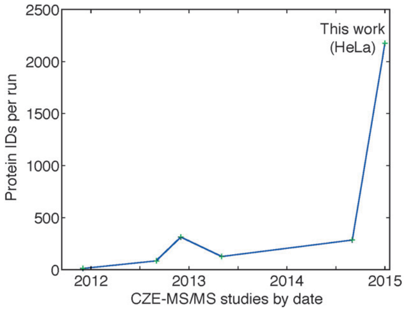
Delivering the goods: Encapsulating liposomes are widely used for controlled drug delivery. Nano-impact experiments are employed for the electrochemical attomolar quantification of the contents of a vitamin C encapsulating liposome at the single liposome level. Liposome sizing and their picomolar concentration are also determined in biological buffer in real time.

Proteomics

L. Sun, A. S. Hebert, X. Yan, Y. Zhao,
M. S. Westphall, M. J. P. Rush, G. Zhu,
M. M. Champion, J. J. Coon,
N. J. Dovichi* ________ **13931 – 13933**

Over 10 000 Peptide Identifications from the HeLa Proteome by Using Single-Shot Capillary Zone Electrophoresis Combined with Tandem Mass Spectrometry

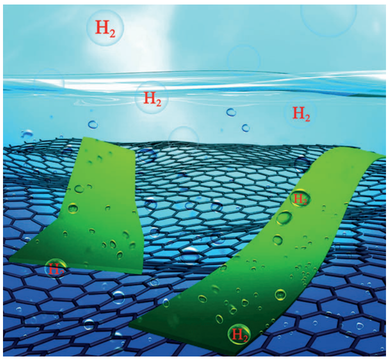
Let's see some ID: 2100 protein and 10 000 peptide identifications (IDs) from a HeLa cell proteome digest were obtained in a single 100 min capillary zone electrophoresis (CZE)–tandem mass spectrometry (MS/MS) analysis. These results represent an almost tenfold improvement in peptide and protein IDs compared with previous single-shot analyses using this technology.



Carbon Materials

Y. Zhao, F. Zhao, X. Wang, C. Xu,
Z. Zhang, G. Shi, L. Qu* _ **13934 – 13939**

Graphitic Carbon Nitride Nanoribbons: Graphene-Assisted Formation and Synergic Function for Highly Efficient Hydrogen Evolution



A non-metallic electrocatalyst: A three-dimensional architecture of in situ formed 1D graphitic carbon nitride nanoribbons on two-dimensional graphene sheets has been prepared (see picture). The compound is a highly efficient electrocatalyst for the hydrogen evolution and shows a low overpotential and an extremely large exchange current density, which is even larger than that of metal catalysts.

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

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

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

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