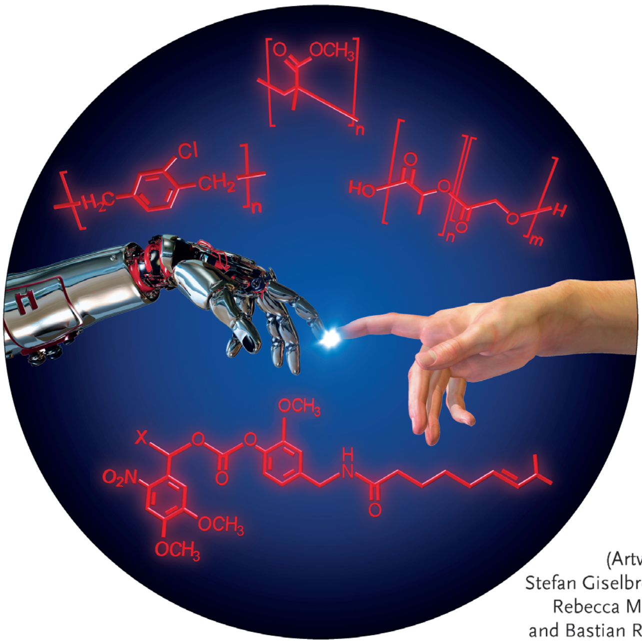
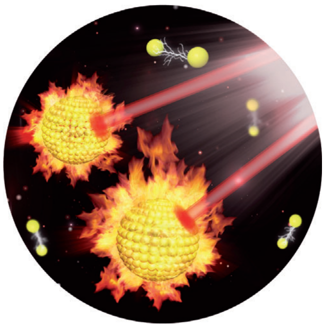
Even after 125 years ...

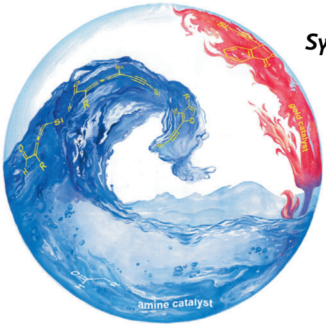

(Artwork:
Stefan Giselbrecht,
Rebecca Meyer,
and Bastian Rapp)

… *Angewandte Chemie* is looking into the future, and in this last issue of the anniversary volume in particular. The cover picture of this issue is for a Review by C. M. Niemeyer et al. (page 13942 ff.) on the chemistry of cyborgs. These cybernetic organisms are chimeras of machines and living organisms. As alluded to by the adaptation of Michelangelo's famous painting, this rapidly emerging field of research and development takes advantage of chemical compounds and concepts, including, but not limited to, biocompatible polymer coatings for implants. Further Reviews are on the plasmonic synthesis of nanoparticles (C. Mirkin et al.) and the generation of pluripotent stem cells (Nobel Lecture by S. Yamanaka).

Theranostics

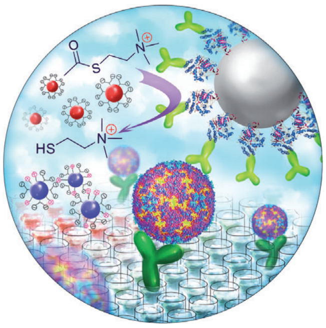
In their Communication on page 13958 ff., Z. Nie, X. Chen, et al. describe plasmonic gold vesicles for the simultaneous thermal/photoacoustic cancer imaging and photothermal therapy. The ultrastrong plasmonic coupling in the vesicles leads to a very high photothermal conversion efficiency.





Synthetic Methods

Y. Huang and co-workers describe in their Communication on page 14219 ff. the principle of synergistic catalysis for promoting an α-vinylidenation or α-vinylidenation/γ-functionalization of aldehydes to generate tri- and tetrasubstituted allenes.



Pathogen Detection

In their Communication on page 14065 ff., X. Chen et al. describe a new colorimetric assay for pathogen detection based on a two-step signal amplification process that allows the results to be observed by the naked eye alone.

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Editorial

"... Since all manuscripts need to be reviewed, the requests for referee reports become increasingly frequent. It becomes impossible to serve all these requests as the scientists also need to do research and teaching and fulfill other duties, depending on their employment at a university, non-university institutions, or in industry ..."
Read more in the Editorial by François Diederich.

Miscellaneous

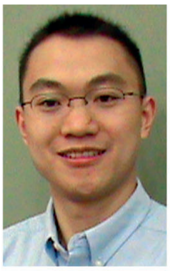
Author Profile

"I would have liked to have discovered olfactory receptors. My favorite food is shrimp. ..."
This and more about Jiangyun Wang can be found on page 13858.

News


F. Krausz


T. Scheibel


Y. R. Chi


K. J. J. Mayrhofer


T. Geelhaar


G. A. Olah


G. K. S. Prakash


A. Brik

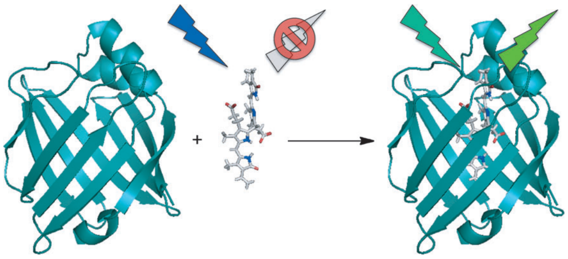

M. Grätzel


H. Kessler

Books

Highlights

Fluorescent Probes



Green light for a new method: The protein UnaG shows bright green fluorescence in conjugation with bilirubin. The high affinity and specificity of UnaG allows for the fast and reliable measurement of bilirubin levels in human serum, which could improve the diagnosis of neonatal jaundice and other disorders based on insoluble bilirubin. UnaG expands the toolbox of fluorescent proteins with new features, such as oxygen independence and fast inducibility.

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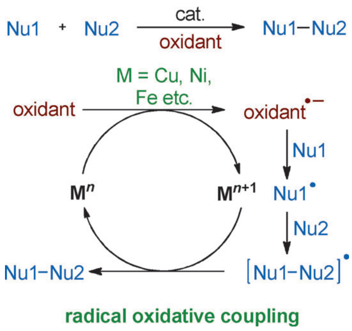
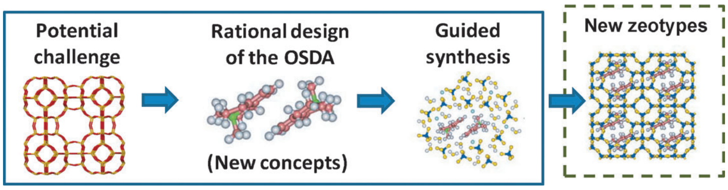


Radicals can do it! Oxidative coupling processes that proceed by a single-electron-transfer mechanism have been established. Recently developed methods demonstrate the ability of non-precious-metal catalysts to act as efficient catalysts for such transformations. This concept provides a sustainable approach for the construction of C–C and C–X bonds.

Essays

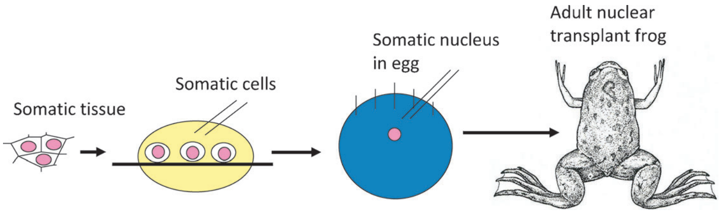
A technological plateau: The pace of technological innovation today is slower than between 1920 and 1960. In this Essay, the evolution of fundamental research since 1920 is examined, with particular emphasis on how fundamental research was carried out in industrial settings, and the effect of national funding agencies on creating marketlike competition in research. This competition was meant to accelerate the speed of innovation and, as a consequence, produce higher economic growth. However, neither of these expectations were met.

Minireviews



Made to measure: Organic structure-directing agents (OSDAs) have led to important advances in zeolite synthesis. The careful choice of OSDA allows the targeted preparation of zeolites with specific physiochemical and catalytic properties, and the synthesis of novel and improved zeolites by similar principles can be expected in the near future.

Reviews



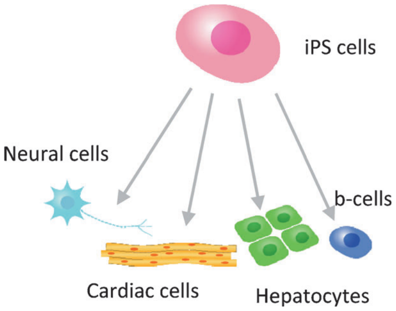
Common somatic cells can be deprogrammed to stem cells, which can grow into all types of tissues. The early phase of this research, which led to the Nobel Prize in 2013, is described first hand by J. B. Gurden in his Nobel Review.

Pluripotent Stem Cells

S. Yamanaka* ———— **13900 – 13909**

The Winding Road to Pluripotency (Nobel Lecture)

The forced expression of certain transcription factors can induce pluripotency in somatic cells. This led to the research and development of effective reprogramming techniques for the generation of induced pluripotent stem cells (iPS cells). S. Yamanaka received the 2012 Nobel Prize in Physiology or Medicine for his research in this area.



Metal Nanoparticles

M. R. Langille, M. L. Personick,
C. A. Mirkin* ———— **13910 – 13940**

Plasmon-Mediated Syntheses of Metallic Nanostructures

Power of the light: Plasmon-mediated synthetic methods are excellent techniques for controlling the growth and final shape of metal nanostructures. These reactions use visible light irradiation and excitation of plasmonic seeds to drive the chemical reduction of metal ions, usually Ag^+, by citrate. The underlying physical and chemical factors that influence structural selection are outlined along with some important design considerations for controlling particle shape.

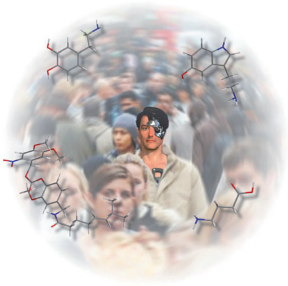
Cybernetics

S. Giselbrecht, B. E. Rapp,
C. M. Niemeyer* ———— **13942 – 13957**

The Chemistry of Cyborgs—Interfacing Technical Devices with Organisms

Front Cover

Cyborgs, modern chimeras of a machine and a living organism, are usually considered to be science-fiction—this is not the case. Recent examples of modern prosthetics, brain–machine interfaces and the evolution of organism/machine hybrids are highlighting how living and artificial systems can be interfaced and how chemistry contributes to these developments.



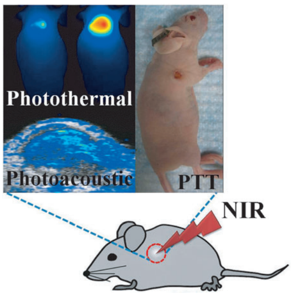
Communications

Theranostics

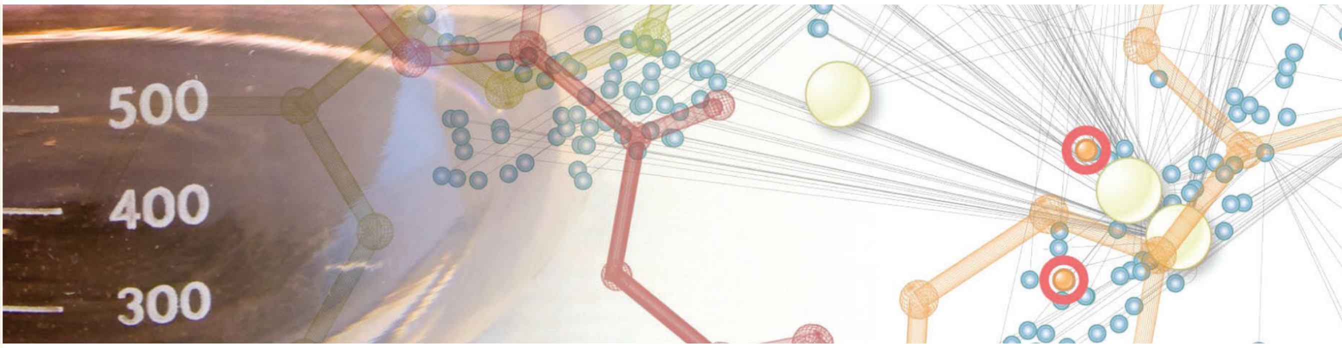
P. Huang, J. Lin, W. Li, P. Rong, Z. Wang,
S. Wang, X. Wang, X. Sun, M. Aronova,
G. Niu, R. D. Leapman, Z. Nie,*
X. Chen* ———— **13958 – 13964**

Biodegradable Gold Nanovesicles with an Ultrastrong Plasmonic Coupling Effect for Photoacoustic Imaging and Photothermal Therapy

Frontispiece



They do their job and clear out: A disulfide-terminated copolymer graft enabled the dense packing of gold nanoparticles (GNPs) into biodegradable plasmonic gold vesicles for simultaneous thermal/photoacoustic cancer imaging and photothermal therapy (PTT; see picture). The ultrastrong plasmonic coupling effect between adjacent GNPs led to a strong near-infrared (NIR) absorption and very high photothermal conversion efficiency ($\eta = 37\%$).



Novartis is pleased to announce the 2013 recipients of the

Novartis Early Career Award in Organic Chemistry

Professor Nicolai Cramer, *EPF Lausanne, Switzerland*

Nicolai Cramer earned his Ph.D. in 2005 in the group of Professor Sabine Laschat at the University of Stuttgart. After a stay with Professors Michio Murata and Sumihiro Hase at Osaka University he joined the group of Professor Barry M. Trost at Stanford University as a postdoctoral fellow. In 2007, he started his habilitation at the ETH Zürich associated to Professor Erick M. Carreira and in 2010 took his current position at EPF Lausanne. Professor Cramer has made major contributions to the field of enantioselective metal-catalyzed transformations and has been a pioneer in the development of catalytic methods for selective functionalization of relatively inert C-H and C-C bonds.

Professor Daniel Rauh, *Technische Universität, Dortmund, Germany*

Daniel Rauh earned his Ph.D. in 2002 from Phillips-Universität Marburg working with Professor Gerhard Klebe. Later that year he spent time as a Research Fellow at the Genomics Institute of the Novartis Research Foundation (GNF) in San Diego. His postdoctoral studies began with Professor Milton Stubbs at Martin-Luther-Universität Halle-Wittenberg and then with Professor Kevan Shokat at the University of California, San Francisco. Professor Rauh started his independent career at Dortmund in 2006 and has made truly innovative contributions to the field of chemical biology in the development of high-throughput assay methodologies for the identification of allosteric kinase inhibitors, and in the creative design of functional probes for targeting proteins and dissecting oncogene dependencies.

The Novartis Early Career Award in Organic Chemistry is presented annually to outstanding scientists within 10 years of having established an independent academic research career, in the areas of organic or bioorganic chemistry in the broadest sense. Two winners are identified, from the Global Research community, each of whom receives an unrestricted research grant.

Past Awardees:

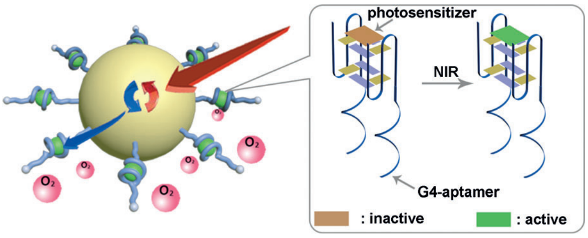
2012	Sarah E. Reisman and Corey R.J. Stephenson
2011	David Chen and David Spiegel
2010	Karl Gademann and Jin-Quan Yu
2009	Christopher J. Chang and Magnus Rueping
2008	Matthew J. Gaunt and Jeffrey S. Johnson
2007	Lukas J. Goossen and Anna K. Mapp
2006	Armido Studer and F. Dean Toste
2005	Benjamin List and Dirk Trauner
2004	J. Stephen Clark and Jonathan P. Clayden
2003	Thorsten Bach
2002	Bernhard Breit and Thomas Carell
2001	Tim Donohoe
2000	Andrew Miller
1999	Alan Armstrong
1998	Mark Bradley

NOVARTIS

Imaging Agents

Q. Yuan, Y. Wu, J. Wang, D. Lu, Z. Zhao, T. Liu, X. Zhang, W. Tan* **13965 – 13969**

Targeted Bioimaging and Photodynamic Therapy Nanoplatform Using an Aptamer-Guided G-Quadruplex DNA Carrier and Near-Infrared Light



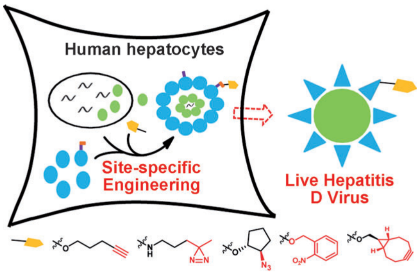
Target practice: A novel photodynamic therapy system has been constructed by taking advantage of the specific molecular recognition of an aptamer, loading capability of a G-quadruplex, and upconversion of nanoparticles using near-infrared (NIR) light. This system selectively delivers a photosensitizer to targeted cells and upon irradiation with NIR light demonstrates phototoxicity effects.

Virus Engineering

S.-X. Lin, H. Yan, L. Li, M.-Y. Yang, B. Peng, S. Chen, W.-H. Li,* P. R. Chen* **13970 – 13974**

Site-Specific Engineering of Chemical Functionalities on the Surface of Live Hepatitis D Virus

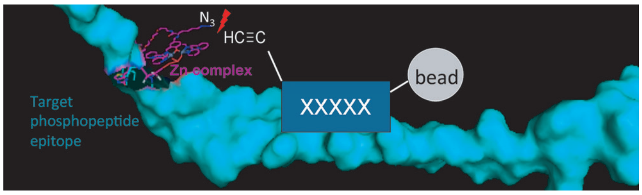
Precise virus labeling: The genetic code expansion strategy was coupled with an engineered virus assembly process in human hepatocytes to produce intact human hepatitis D virus (HDV) bearing a genetically encoded unnatural amino acid. The resultant HDV virions, with one type of five different pyrrolysine analogues introduced site-specifically into virus surface proteins, exhibited near wild-type viability and infectivity.



Click Chemistry

A. Nag, S. Das, M. B. Yu, K. M. Deyle, S. W. Millward, J. R. Heath* **13975 – 13979**

A Chemical Epitope-Targeting Strategy for Protein Capture Agents: The Serine 474 Epitope of the Kinase Akt2



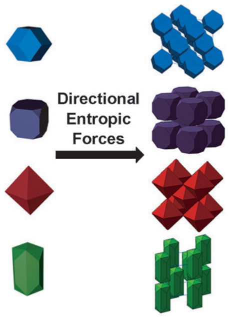
Target and click: Peptide ligands targeted to the C-terminal motif of the kinase Akt2 were obtained by combining phosphate recognition of a dinuclear zinc(II) complex with in situ click chemistry to target this epitope. The peptide ligands (shown as XXXXX) selectively bind the C-terminal polypeptide of Akt2, and are selective for Akt2 relative to the Akt1 and Akt3 isoforms. The ligands differentially modulate Akt2 activity.

Nanoparticle Assemblies

K. L. Young, M. L. Personick, M. Engel, P. F. Damasceno, S. N. Barnaby, R. Bleher, T. Li, S. C. Glotzer,* B. Lee,* C. A. Mirkin* **13980 – 13984**

A Directional Entropic Force Approach to Assemble Anisotropic Nanoparticles into Superlattices

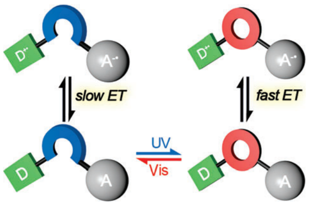
Not touching but sticking: By using cationic surfactant micelles as depletants, a directional entropic force approach (DEFA) assembles anisotropic nanoparticles into superlattices in solution. The micelles induce the face-to-face stacking of the nanoparticles to maximize the system's entropy. The shape of the nanoparticles determines the symmetry of the superlattice, the interparticle spacing is determined by the charged surfactant.



Artificial Photosynthesis

S. Castellanos, A. A. Vieira, B. M. Illescas,
V. Sacchetti, C. Schubert, J. Moreno,
D. M. Guldi,* S. Hecht,*
N. Martín* ———— 13985 – 13990

Gating Charge Recombination Rates through Dynamic Bridges in Tetrathiafulvalene–Fullerene Architectures

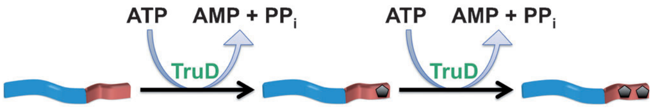


An open and shut case: The competition between charge separation and recombination in artificial photosynthetic systems can be controlled by using photochromic dynamic bridge. The photoinduced opening and closing of the bridge mediates the electronic coupling between donor (D) and acceptor (A).

Adenylation

J. Koehnke, A. F. Bent, D. Zollman,
K. Smith, W. E. Houssen, X. Zhu,
G. Mann, T. Lebl, R. Scharff, S. Shirran,
C. H. Botting, M. Jaspars,
U. Schwarz-Linek,
J. H. Naismith* ———— 13991 – 13996

The Cyanobactin Heterocyclase Enzyme: A Processive Adenylase That Operates with a Defined Order of Reaction

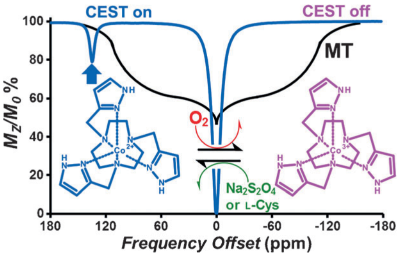


Counting backwards: The cyanobactin class of heterocyclases, exemplified by TruD, possess an almost unique combination of processivity, specificity, chemical versatility, and promiscuity. TruD is shown by biochemical assay to be an adenylase, and processes cysteines in a defined order. The entire substrate leader can be removed and TruD will process a single specific cysteine residue; however the role of leader is to permit processivity through a balance of recognition. ATP/AMP = adenosine tri/monophosphate; PPi = pyrophosphate.

Imaging Agents

P. B. Tsitovich, J. A. Spernyak,
J. R. Morrow* ———— 13997 – 14000

A Redox-Activated MRI Contrast Agent that Switches Between Paramagnetic and Diamagnetic States

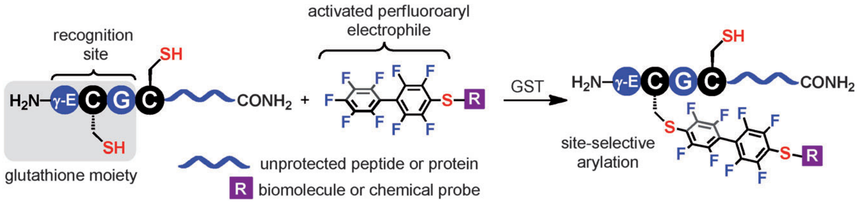


Trigger ready: A redox-activated MRI contrast agent can cycle between paramagnetic Co^{II} (MRI-active) and diamagnetic Co^{III} (MRI-silent). The paramagnetic Co^{II} form produces a highly shifted CEST signal at 135 ppm (37 °C). The redox state of the Co complex is altered by O_2 partial pressure and reductant concentration (thiols) on a time scale relevant to imaging. MT = magnetization transfer.

Bioconjugation

C. Zhang, A. M. Spokoyny, Y. Zou,
M. D. Simon,
B. L. Pentelute* ———— 14001 – 14005

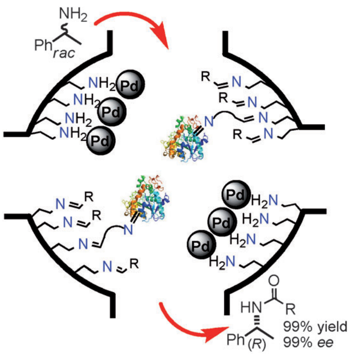
Enzymatic "Click" Ligation: Selective Cysteine Modification in Polypeptides Enabled by Promiscuous Glutathione S-Transferase



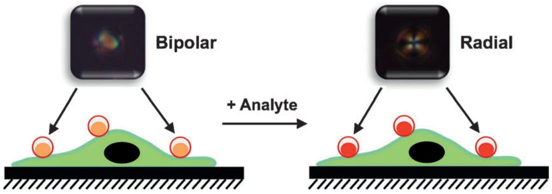
Singled out for special treatment: Naturally occurring glutathione S-transferase (GST) was used to catalyze an efficient "click" ligation between polypeptides with an N-terminal glutathione sequence and biomolecules or chemical probes containing perfluorinated aromatic groups (see scheme). The site-specific modification of one cysteine residue was possible in the presence of other unprotected cysteine residues and reactive functional groups.

Hybrid Catalysts

Surpassing nature: A hybrid catalyst in which *Candida antarctica* lipase B and a nanopalladium species are co-immobilized into the compartments of mesoporous silica is presented. The metal nanoparticles and the enzyme are in close proximity to one another in the cavities of the support. The catalyst mimics a metalloenzyme and was used for dynamic kinetic resolution of a primary amine in high yield and excellent enantioselectivity.

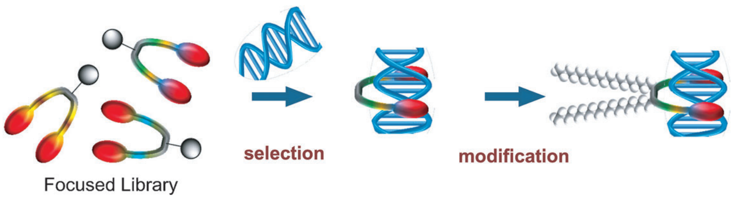


Sensors



I'm stuck on you: Droplet-based liquid crystal (LC) chemical sensors can be immobilized on living cells. The decorated cells can report in real time on the presence of toxins in surrounding culture media. The approach provides new principles for the design of droplet-based LC sensors as well as methods for the local detection and reporting of chemical agents that are difficult to achieve in cellular environments using free-floating LC droplets.

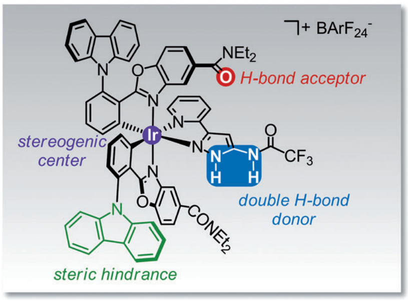
Focused Libraries

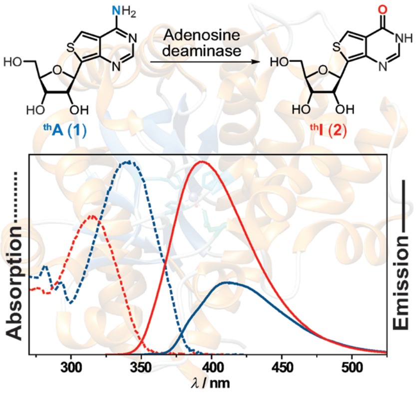


Into the library: Screening a focused library of 259 peptide tweezers, composed of two identical arms with zero to three amino acids and an artificial anion recognition site, yielded DNA binders with nanomolar affinity. These ligands are only modest gene carriers (transfection efficiency < 10%); however, excellent transfection efficiencies (up to 90%) were achieved after the covalent attachment of long aliphatic chains.

Asymmetric Catalysis

Metal-templated organocatalysis: The enantioselective formation of an all-carbon quaternary stereocenter is catalyzed by the ligand sphere of an inert biscyclometalated iridium complex (see picture). In this complex, the metal-centered chirality serves as the sole source for the effective asymmetric induction.



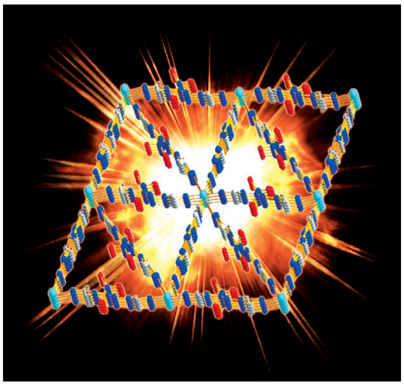


Adenosine deaminase (ADA), a major enzyme involved in purine metabolism, converts an isomorphic fluorescent analogue of adenosine (thA) into an isomorphic inosine analogue (thI), which possesses distinct spectral features, allowing one to monitor the enzyme-catalyzed reaction and its inhibition in real time. The utility of this sensitive fluorescence-monitored transformation for the high-throughput detection and analysis of ADA inhibitors is demonstrated.

Fluorescent Nucleosides

R. W. Sinkeldam, L. S. McCoy, D. Shin, Y. Tor* ______ **14026 – 14030**

Enzymatic Interconversion of Isomorphic Fluorescent Nucleosides: Adenosine Deaminase Transforms an Adenosine Analogue into an Inosine Analogue



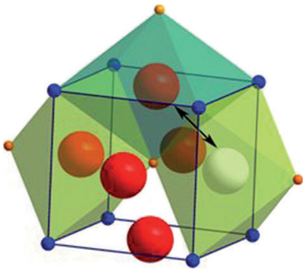
Energetic 3D MOFs: A structurally unique class of three-dimensional energetic metal–organic frameworks (MOFs) was successfully synthesized and characterized. These MOFs have a good thermal stability and a low sensitivity to impact, friction, and electrostatic discharge. The depicted 3D porous MOF shows the unprecedented heat of detonation of 3.62 kcal g^{-1}.

Energetic Materials

S. Li, Y. Wang, C. Qi, X. Zhao, J. Zhang, S. Zhang, S. Pang* ______ **14031 – 14035**

3D Energetic Metal–Organic Frameworks: Synthesis and Properties of High Energy Materials

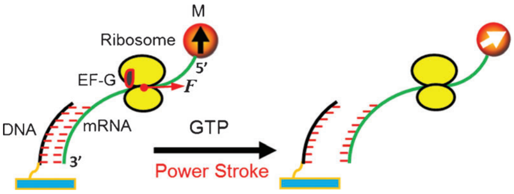
The novel perovskite material, $SrSc_{0.175}Nb_{0.025}Co_{0.8}O_{3-\delta}$, shows a rapid bulk oxygen diffusion rate below 550 °C (see oxygen movement indicated by the black arrow). Incorporation as an oxygen reduction cathode into a samarium-doped ceria fuel cell enables exceptionally high electrochemical performance, indicated by a power density of 910 mW cm^{-2} at 500 °C.



Elektrocatalysis

W. Zhou,* J. Sunarso, M. W. Zhao, F. L. Liang, T. Klande, A. Feldhoff* ______ **14036 – 14040**

A Highly Active Perovskite Electrode for the Oxygen Reduction Reaction Below 600 °C



The power stroke of a motor protein: The motor protein EF-G generates a power stroke of 89 pN during ribosome translocation (see picture). This mechanical force is obtained by measuring the force-induced dissociation of a series of DNA–mRNA duplexes. The dissociation is indicated by a decrease in magnetic signal.

Force Spectroscopy

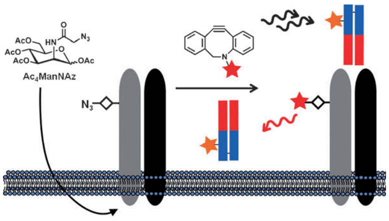
L. Yao, Y. Li, T.-W. Tsai, S. Xu,* Y. Wang* ______ **14041 – 14044**

Noninvasive Measurement of the Mechanical Force Generated by Motor Protein EF-G during Ribosome Translocation

Imaging Glycosylation

B. Belardi, A. de la Zerda, D. R. Spiciarich, S. L. Maund, D. M. Peehl, C. R. Bertozzi* ______ 14045 – 14049

Imaging the Glycosylation State of Cell Surface Glycoproteins by Two-Photon Fluorescence Lifetime Imaging Microscopy

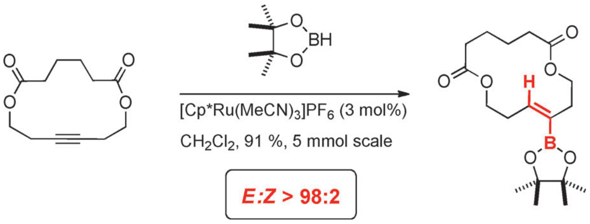


Glycoproteins in focus: Metabolic labeling of glycans with azido sugars (see picture) in combination with two-photon fluorescence lifetime imaging microscopy enables the visualization of specific glycoforms of endogenous proteins. This method can be utilized to detect glycosylated proteins in both cell culture and intact human tissue slices.

Hydroboration

B. Sundararaju, A. Fürstner* ______ 14050 – 14054

A *trans*-Selective Hydroboration of Internal Alkynes

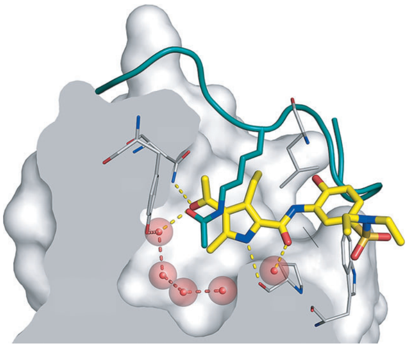


Violate the rule: The reigning stereochemical principle of hydroboration is the suprafacial delivery of hydrogen and boron to the same π-face of a given starting material. This fundamental rule of *cis* addition is now easily broken for internal alkynes with the help of [Cp*Ru(MeCN)$_3$]PF$_6$ (Cp* = η^5-C$_5$Me$_5$) as the catalyst. The resulting *trans*-selective hydroboration opens a practical new entry into *E*-configured alkenylboron derivatives.

Drug Design in Epigenetics

X. Lucas, D. Wohlwend, M. Hügle, K. Schmidtkunz, S. Gerhardt, R. Schüle, M. Jung, O. Einsle, S. Günther* ______ 14055 – 14059

4-Acyl Pyrroles: Mimicking Acetylated Lysines in Histone Code Reading

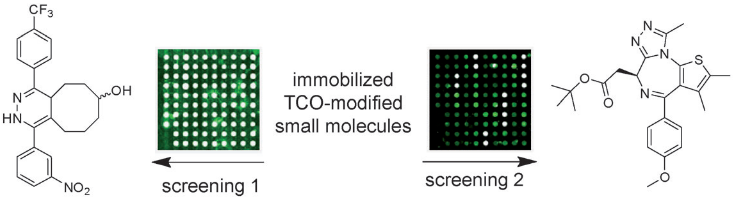


Bromodomains are acetyllysine epigenetic mark reader proteins. Small molecules inhibiting them have potential as anti-inflammatory, antiviral, and anticancer agents. A 4-acyl pyrrole derivative (see yellow structure in recognition pocket) has been identified that potently inhibits specific bromodomains and exhibits antiproliferative activity against leukemia cell lines.

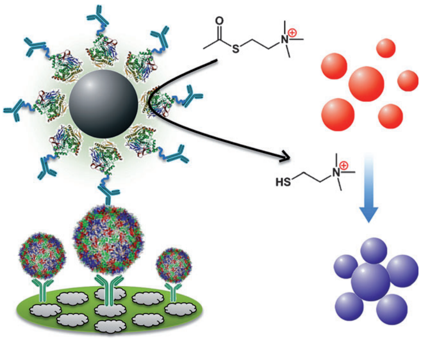
Small-Molecule Microarrays

C.-J. Zhang, C. Y. J. Tan, J. Ge, Z. Na, G. Y. J. Chen, M. Uttamchandani, H. Sun, S. Q. Yao* ______ 14060 – 14064

Preparation of Small-Molecule Microarrays by *trans*-Cyclooctene Tetrazine Ligation and Their Application in the High-Throughput Screening of Protein–Protein Interaction Inhibitors of Bromodomains



Fast and efficient: A library of *trans*-cyclooctene (TCO)-modified small molecules were immobilized on tetrazine-functionalized glass slides by using the fastest bioorthogonal reaction known. The resulting small-molecule microarray was screened against a variety of human bromodomains to identify protein–protein interaction inhibitors.



Seeing is believing: A rapid diagnostic platform for pathogen detection based on the acetylcholinesterase-catalyzed hydrolysis reaction has been developed. Owing to signal amplification strategies, the sensitivity of this assay is comparable to that of PCR. In addition, the readout of the assay is based on solution color change, which can be easily observed by the naked eye alone.

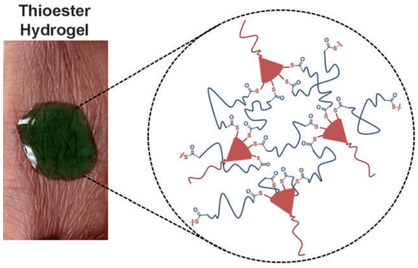
Pathogen Detection

D. Liu, Z. Wang, A. Jin, X. Huang, X. Sun, F. Wang, Q. Yan, S. Ge, N. Xia, G. Niu, G. Liu, A. R. Hight Walker, X. Chen* **14065 – 14069**

Acetylcholinesterase-Catalyzed Hydrolysis Allows Ultrasensitive Detection of Pathogens with the Naked Eye

Back Cover

Washable wound dressing: A dissolvable dendritic thioester hydrogel for wound closure has been developed. The hydrogel sealant adheres strongly to tissues, closes an ex vivo vein puncture, and withstands high pressures placed on a wound. This material can be washed off upon exposure to thiolates because a thiol–thioester exchange takes place, and gradual wound re-exposure may be achieved during surgical care.

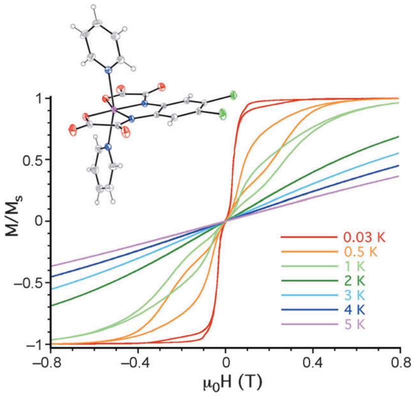


Hydrogels

C. Ghobril, K. Charoen, E. K. Rodriguez, A. Nazarian, M. W. Grinstaff* **14070 – 14074**

A Dendritic Thioester Hydrogel Based on Thiol–Thioester Exchange as a Dissolvable Sealant System for Wound Closure

There is plenty of room at the bottom: A gap in the literature of molecular nanomagnets has been filled with the preparation of the first mononuclear manganese(III) complex exhibiting a slow relaxation of the magnetization, that is, a species with a single slow-relaxing, highly anisotropic Mn^{III} ion, as confirmed by very low-temperature micro-SQUID magnetization and high-field EPR spectroscopic measurements (N blue, O red, Mn purple, Cl green).

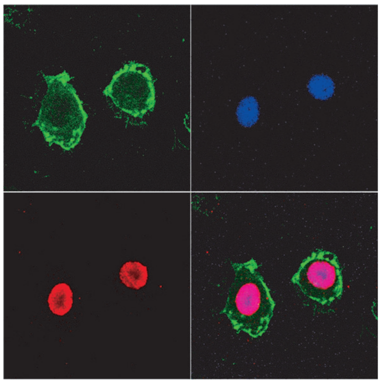


Molecular Nanomagnets

J. Vallejo, A. Pascual-Álvarez, J. Cano,* I. Castro, M. Julve, F. Lloret, J. Krzystek, G. De Munno, D. Armentano,* W. Wernsdorfer, R. Ruiz-García, E. Pardo* **14075 – 14079**

Field-Induced Hysteresis and Quantum Tunneling of the Magnetization in a Mononuclear Manganese(III) Complex

An enhanced suppression system enables the expression of proteins in mammalian cells incorporating one unnatural amino acid (UAA) into multiple sites, as well as two different UAAs into distinct sites in a protein of interest. The utility of this technology was demonstrated by generating a full-length antibody, site-specifically conjugated to a drug and a fluorophore, and characterizing its activity in vitro (see picture).



Gene Technology

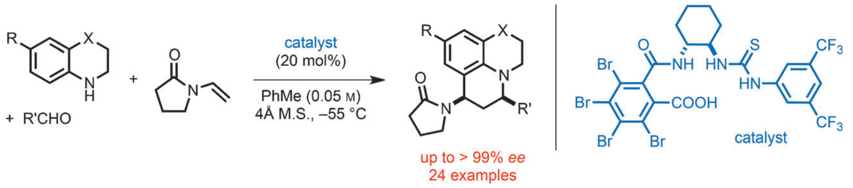
H. Xiao, A. Chatterjee, S. Choi, K. M. Bajjuri, S. C. Sinha, P. G. Schultz* **14080 – 14083**

Genetic Incorporation of Multiple Unnatural Amino Acids into Proteins in Mammalian Cells

Organocatalysis

C. Min, N. Mittal, D. X. Sun,
D. Seidel* ———— 14084 – 14088

Conjugate-Base-Stabilized Brønsted Acids as Asymmetric Catalysts: Enantioselective Povarov Reactions with Secondary Aromatic Amines

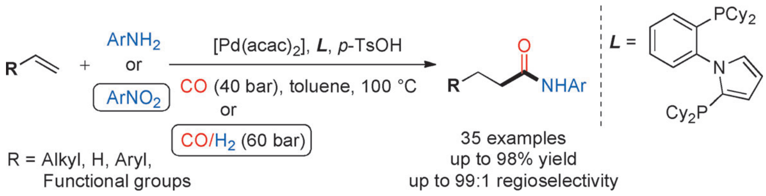


Caught in the act: A new concept for asymmetric Brønsted acid catalysis is presented. Compounds containing an acidic functionality in addition to an anion recognition site act as powerful conjugate-base-stabilized Brønsted acid catalysts. This strategy was applied to the first catalytic enantioselective three-component Povarov reaction of indoline and other secondary aromatic amines (see scheme; M.S. = molecular sieves).

Carbonylation

X. Fang, R. Jackstell,
M. Beller* ———— 14089 – 14093

Selective Palladium-Catalyzed Aminocarbonylation of Olefins with Aromatic Amines and Nitroarenes

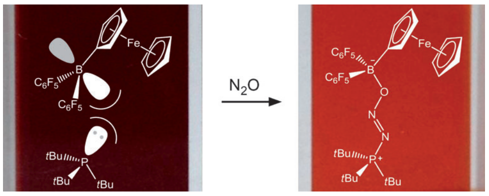


Various olefins can be smoothly transformed in the presence of a Pd-based catalyst system and (hetero)aromatic amines or nitroarenes to synthetically interesting amides in good yields and often with high regioselectivity (see scheme). Combining this atom-efficient procedure with established functionalizations of the resulting products allows the efficient preparation of quinolines.

Nitrous Oxide Detection

M. J. Kelly, J. Gilbert, R. Tirfoin,
S. Aldridge* ———— 14094 – 14097

Frustrated Lewis Pairs as Molecular Receptors: Colorimetric and Electrochemical Detection of Nitrous Oxide

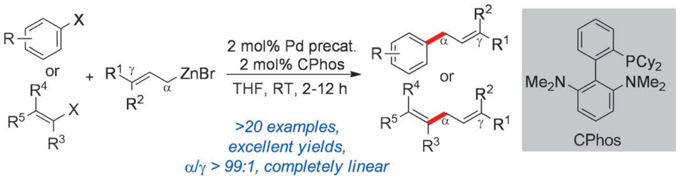


Laughing about frustration: Frustrated Lewis pairs comprising a bulky tertiary phosphine and a strongly Lewis acidic ferrocenyl borane ($FcB(C_6F_5)_2$) have been investigated for the colorimetric/electrochemical detection of N_2O. One such system, based on $tBu_3P/FcB(C_6F_5)_2$, not only signals the presence of N_2O, but also has the ability to differentiate between N_2O and O_2.

Selective Cross-Coupling

Y. Yang, T. J. L. Mustard, P. H.-Y. Cheong,*
S. L. Buchwald* ———— 14098 – 14102

Palladium-Catalyzed Completely Linear-Selective Negishi Cross-Coupling of Allylzinc Halides with Aryl and Vinyl Electrophiles

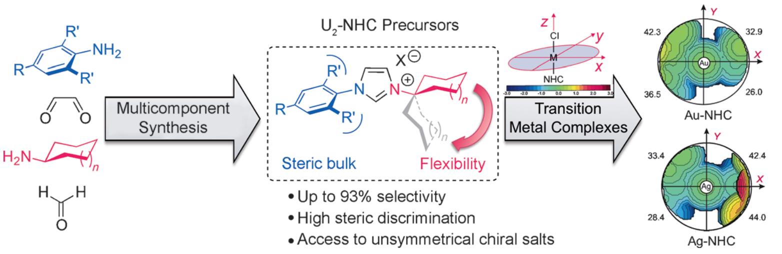


Completely linear: The title reaction provides an effective means to access a wide range of prenylated arenes and "skipped dienes" in a completely linear-selective fashion, as demonstrated by a concise synthesis of the anti-HIV natural product siamenol. DFT calculations shed light on the origin of the excellent regioselectivity observed with the current Pd-based catalyst system.

NHC Ligand Synthesis

P. Queval, C. Jahier, M. Rouen, I. Artur,
J.-C. Legeay, L. Falivene, L. Toupet,
C. Crévisy, L. Cavallo, O. Baslé,*
M. Mauduit* ________ **14103 – 14107**

Multicomponent Synthesis of Unsymmetrical Unsaturated N-Heterocyclic Carbene Precursors and Their Related Transition-Metal Complexes



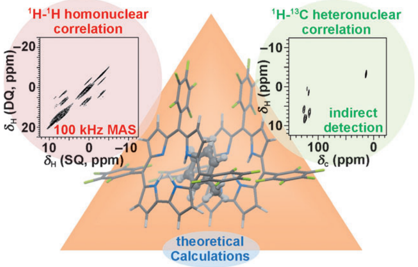
A low-cost, modular, and easily scalable multicomponent procedure, affording access to a wide range of (a)chiral unsymmetrical 1-aryl-3-cycloalkyl-imidazolium salts in good yields and excellent selectivities, is disclosed. Electronic and steric properties of the corresponding unsymmetrical unsaturated N-heterocyclic carbene (U_2-NHC) ligands were evaluated and evidenced strong electron-donor ability, high steric discrimination, and modular steric demand.

NMR Spectroscopy

T. Kobayashi, K. Mao, P. Paluch,
A. Nowak-Król, J. Sniechowska,
Y. Nishiyama, D. T. Gryko,
M. J. Potrzebowski,*
M. Pruski* ________ **14108 – 14111**

Study of Intermolecular Interactions in the Corrole Matrix by Solid-State NMR under 100 kHz MAS and Theoretical Calculations

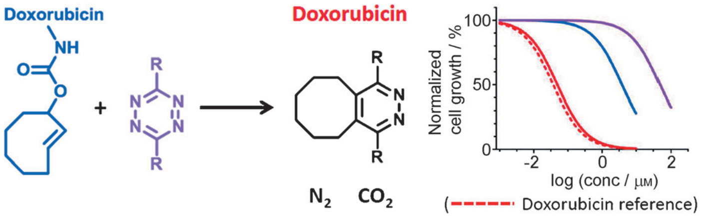
A combination of solid-state NMR techniques and theoretical calculations confirmed that unsubstituted metal-free corroles form supramolecular systems with toluene through π–π interactions in the solid state. Ultrafast magic angle spinning (MAS) enabled the use of ^{1}H–^{1}H homonuclear correlation spectroscopy to explore those intermolecular interactions for which heteronuclear correlation methods were difficult to apply.



Bioorthogonal Reactions

R. M. Versteegen, R. Rossin,
W. ten Hoeve, H. M. Janssen,
M. S. Robillard* ________ **14112 – 14116**

Click to Release: Instantaneous Doxorubicin Elimination upon Tetrazine Ligation



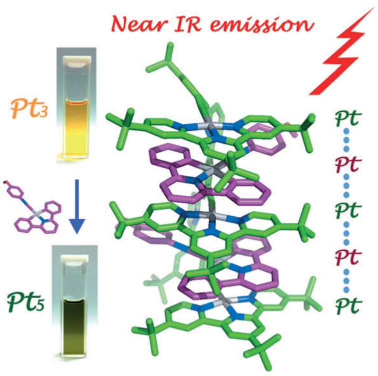
Eliminated without a trace: The fastest click reaction, the highly selective inverse-electron-demand Diels–Alder reaction, has been modified to enable selective bioorthogonal release. Thus, the click reaction of a tetrazine with a drug-bound *trans*-cyclooctene caused the instantaneous release of the drug and CO_2 (see scheme). One possible application is the chemically triggered release, and thereby activation, of a drug from a tumor-bound antibody–drug conjugate.

Supramolecular Assemblies

Y. Tanaka, K. M.-C. Wong,
V. W.-W. Yam* ________ 14117 – 14120

Platinum-Based Phosphorescent Double-Decker Tweezers: A Strategy for Extended Heterologous Metal–Metal Interactions

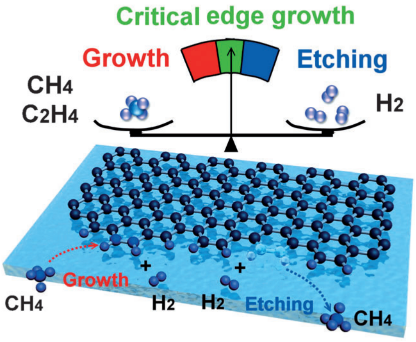
Double sandwich: Phosphorescent molecular double-decker tweezers based on an alkynyl platinum(II) terpyridine system have been synthesized. The tweezers can accommodate two platinum guest complexes, giving rise to drastic color changes (see picture) and near-IR emissions as a result of extended $Pt^{II}\cdots Pt^{II}$ interactions.



Nanomaterials

D. Wei,* Y. Lu, C. Han, T. Niu, W. Chen,
A. T. S. Wee* ________ 14121 – 14126

Critical Crystal Growth of Graphene on Dielectric Substrates at Low Temperature for Electronic Devices

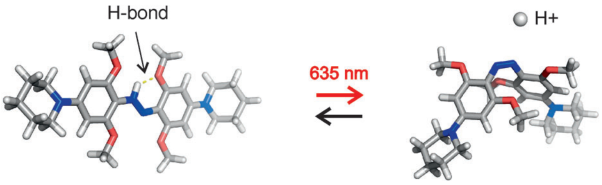


Born at its final resting place: Moderate etching by a hydrogen plasma during plasma-enhanced chemical vapor deposition led to a critical equilibrium state of graphene edge growth in which graphene hexagonal single crystals or continuous graphene films were produced directly on dielectric substrates at 400 °C without a catalyst (see picture). The direct use of the resulting high-quality graphene in devices avoids troublesome transfer processes.

Photoisomerism

S. Samanta, A. Babalhavaeji, M.-x. Dong,
G. A. Woolley* ________ 14127 – 14130

Photoswitching of *ortho*-Substituted Azonium Ions by Red Light in Whole Blood

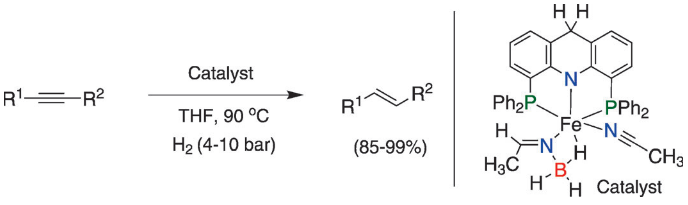


Red-light switches: Tetra-*ortho*-methoxy substituted aminoazobenzenes form azonium ions at neutral pH, isomerize to the *cis* form when illuminated with red light (635 nm), and relax thermally to the *trans* form on a timescale of seconds.

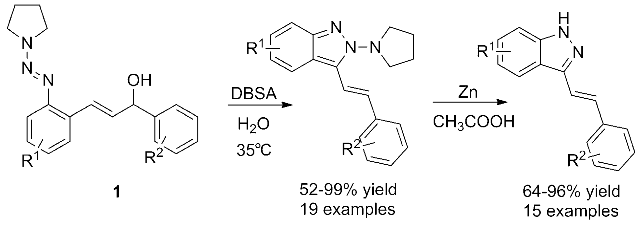
Iron Catalysis

D. Srimani, Y. Diskin-Posner, Y. Ben-David,
D. Milstein* ________ 14131 – 14134

Iron Pincer Complex Catalyzed, Environmentally Benign, *E*-Selective Semi-Hydrogenation of Alkynes



Ironing out hydrogenation: For the first time, an iron catalyst provided chemo- and stereo-selective semi-hydrogenation of alkynes to *E*-alkenes. This efficient, atom-economical reaction is catalyzed by a novel acridine-based PNP iron pincer catalyst and exhibits excellent functional group tolerance under mild, neutral, environmentally benign reaction conditions.

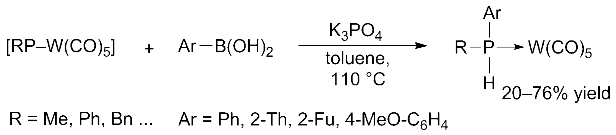


Testing the waters: An efficient dodecyl benzene sulfonic acid (DBSA) catalyzed approach to the synthesis of the title compounds in water is reported. Furthermore, upon cleavage of the pyrrolidine group from the *trans*-3-alkenyl-2-pyrrolidine-2*H*-indazoles with Zn in CH$_3$COOH, *trans*-3-alkenyl-1*H*-indazoles are obtained in good to excellent yields.

Heterocycles

W. Yang, Z. Yang, L. Xu, L. Zhang, X. Xu, M. Miao, H. Ren* ——— **14135 – 14139**

Surfactant-Type Brønsted Acid Catalyzed Stereoselective Synthesis of *trans*-3-Alkenyl Indazoles from Triazenylaryl Allylic Alcohols in Water

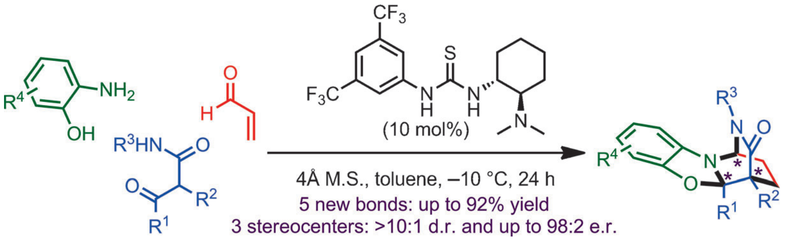


User friendly P–C: Electrophilic terminal phosphinidene complexes [RP–W(CO)$_5$] react with Ar–B(OH)$_2$ to give the corresponding secondary phosphine complexes [{R(Ar)PH}W(CO)$_5$]. This method enables the formation of P–C bonds through the combination of a wide array of heterocyclic and aryl boronic acids with various electrophilic phosphinidene complexes. The final products incorporate a P–H bond that can be used for further transformations.

Phosphinidene Complexes

Y. X. Ng, F. Mathey* ——— **14140 – 14142**

Using Monovalent Phosphorus Compounds to Form P–C Bonds

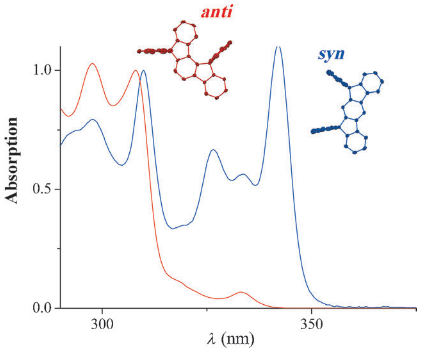


Three-star compounds: The title reaction of β-ketoamides, acrolein, and aminophenols, catalyzed by a bifunctional thiourea-tertiary amine organocatalyst, enables the preparation of an enantioenriched diazabicyclo[2.2.2]octanone (2,6-DABCO) scaffold. The chemoselective reaction sequence installs five new bonds and three stereocenters, two of which are contiguous tetrasubstituted centers, with excellent yields and high levels of stereocontrol. M.S. = molecular sieves.

Heterocycles

M. M. Sanchez Duque, O. Baslé, Y. Génisson, J.-C. Plaquevent, X. Bugaut,* T. Constantieux,* J. Rodriguez ——— **14143 – 14146**

Enantioselective Organocatalytic Multicomponent Synthesis of 2,6-Diazabicyclo[2.2.2]octanones



Taking pole position: The relative position of the ring bridging has a unique and remarkable effect on the spectroscopic properties of dihydroindeno[1,2-*a*]/[2,1-*b*]fluorenes (see picture). These blue-emitting positional isomers have been successfully used as the emitting layer in organic light-emitting diodes (OLEDs), with performance among the highest reported for dihydroindenofluorene-based OLEDs.

Organic Semiconductors

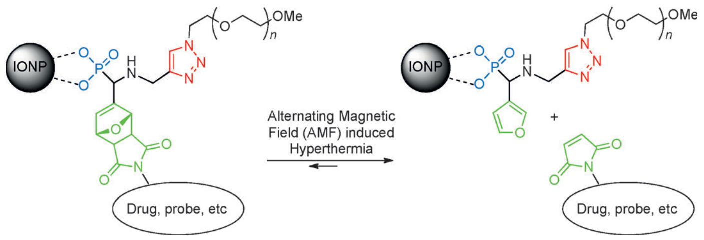
M. Romain, D. Tondelier, J.-C. Vanel, B. Geffroy, O. Jeannin, J. Rault-Berthelot, R. Métivier, C. Poriel* ——— **14147 – 14151**

Dependence of the Properties of Dihydroindenofluorene Derivatives on Positional Isomerism: Influence of the Ring Bridging

Functional Nanoparticles

T. T. T. N'Guyen, H. T. T. Duong, J. Basuki, V. Montembault, S. Pascual, C. Guibert, J. Fresnais, C. Boyer, M. R. Whittaker, T. P. Davis, L. Fontaine* **14152 – 14156**

Functional Iron Oxide Magnetic Nanoparticles with Hyperthermia-Induced Drug Release Ability by Using a Combination of Orthogonal Click Reactions

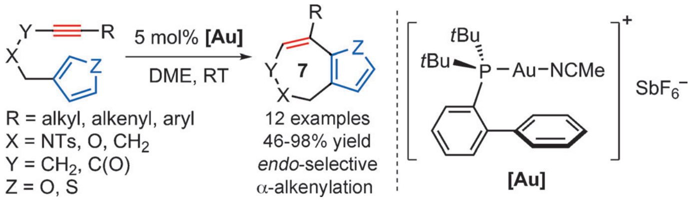


Click and drug: A combination of orthogonal click reactions is employed for the preparation of functional iron oxide nanoparticles (IONPs) that show unprecedented hyperthermia-induced drug release through a magnetically stimulated retro-Diels–Alder (rDA) process. Magnetic stimulation induces sufficient local energy in close proximity to the cycloadduct to initiate the rDA process.

Gold Catalysis

Z. Dong, C.-H. Liu, Y. Wang, M. Lin, Z.-X. Yu* **14157 – 14161**

Gold(I)-Catalyzed *endo*-Selective Intramolecular α-Alkenylation of β-Yne-Furans: Synthesis of Seven-Membered-Ring-Fused Furans and DFT Calculations

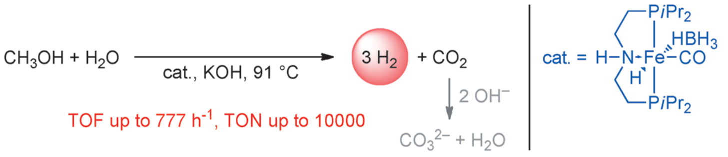


Alkenylation of furans: An efficient gold-catalyzed *endo*-selective intramolecular α-alkenylation of β-alkyne-substituted furans has been developed to synthesize challenging seven-membered-ring-fused furans in good to excellent yields. Preliminary DFT calculations have been carried out to understand the experimentally observed regioselectivity. DME = 1,2-dimethoxyethane, Ts = *p*-toluenesulfonyl.

Renewable Energy

E. Alberico, P. Sponholz, C. Cordes, M. Nielsen, H.-J. Drexler, W. Baumann, H. Junge, M. Beller* **14162 – 14166**

Selective Hydrogen Production from Methanol with a Defined Iron Pincer Catalyst under Mild Conditions

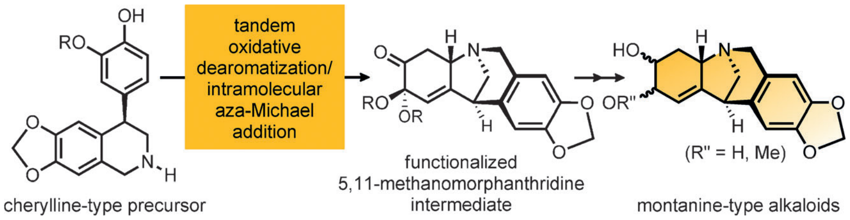


Ironing out the hydrogen: A molecularly defined iron pincer complex is able to catalyze the dehydrogenation of aqueous methanol at low temperatures. This represents a further step towards the implementation of a "methanol/hydrogen economy".

Asymmetric Synthesis

X. Bao, Y.-X. Cao, W.-D. Chu, H. Qu, J.-Y. Du, X.-H. Zhao, X.-Y. Ma, C.-T. Wang, C.-A. Fan* **14167 – 14172**

Bioinspired Total Synthesis of Montanine-Type *Amaryllidaceae* Alkaloids

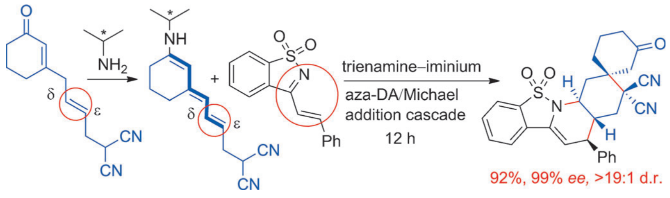


Finding a common path: A synthetic strategy inspired by the proposed biogenesis of the montanine-type alkaloids enabled the concise asymmetric synthesis of these compounds in a divergent fashion on the basis of an unprecedented tandem oxidative dearomatization/intramolecular aza-Michael addition as the key step. This bioinspired approach revealed a chemical connection between the cherylline- and montanine-type alkaloids (see scheme).

Organocatalysis

X. Feng, Z. Zhou, C. Ma, X. Yin, R. Li,*
L. Dong, Y.-C. Chen* ——— **14173 – 14176**

Trienamines Derived from Interrupted Cyclic 2,5-Dienones: Remote δ,ε-C=C Bond Activation for Asymmetric Inverse-Electron-Demand Aza-Diels–Alder Reaction

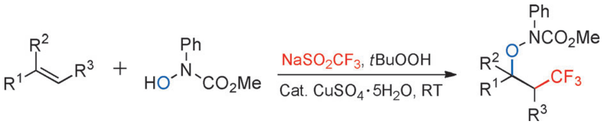


Newly framed: The δ,ε C=C bond of an interrupted cyclic 2,5-dienone induces the formation of a linear trienamine in the presence of a chiral primary amine, thus enabling the δ,ε-C=C bond to participate in a highly asymmetric inverse-electron-demand aza-Diels–Alder (DA) reaction with electron-deficient 1-azadienes. The DA reaction can be coupled with a Michael addition to produce a polycyclic framework with complete stereocontrol.

Synthetic Methods

X.-Y. Jiang, F.-L. Qing* ——— **14177 – 14180**

Copper-Catalyzed Three-Component Oxytrifluoromethylation of Alkenes with Sodium Trifluoromethanesulfinate and Hydroxamic Acid

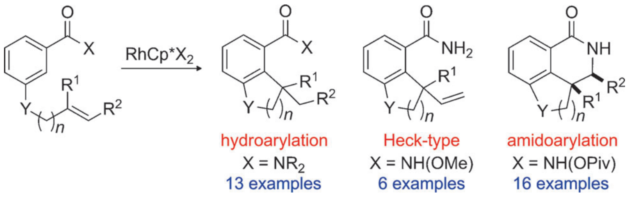


Radical paths: The title reaction of olefins with $NaSO_2CF_3$ and *N*-hydroxy-*N*-phenylacetamide at room temperature is described for the first time (see scheme). This reaction provides a practical and convenient route to a series of trifluoromethylated alcohols bearing a wide range of functional groups.

Rhodium Catalysis

T. A. Davis, T. K. Hyster,
T. Rovis* ——— **14181 – 14185**

Rhodium(III)-Catalyzed Intramolecular Hydroarylation, Amidoarylation, and Heck-type Reaction: Three Distinct Pathways Determined by an Amide Directing Group

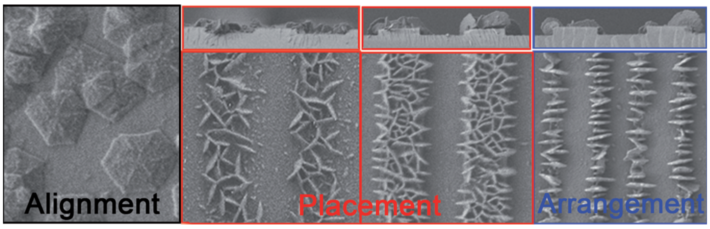


The amide decides: Three different rhodium(III)-catalyzed reaction pathways of a wide variety of tethered alkenes can be accessed through changing the amide directing group. This provides an efficient route to a myriad of complex polycyclic products, many containing newly formed all-carbon quaternary centers. Amidoarylations can diastereoselectively deliver products with up to three contiguous stereocenters.

Oriented Self-Assembly

B. Liu, Y. Yao, S. Che* ——— **14186 – 14190**

Template-Assisted Self-Assembly: Alignment, Placement, and Arrangement of Two-Dimensional Mesostructured DNA–Silica Platelets

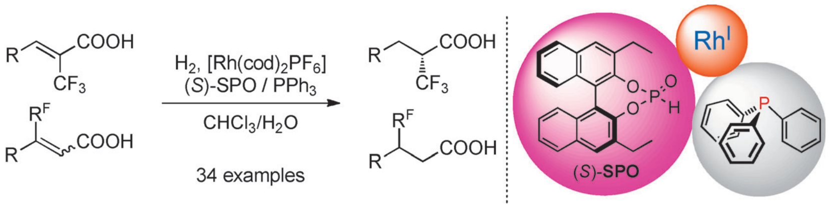


In the same direction: Two-dimensional mesostructured DNA–silica platelets were horizontally or vertically aligned on unpatterned substrate surfaces using "bottom-up" self-assembly. Through template-assisted self-assembly, vertically aligned DNA–silica platelets were selectively placed in the grooves and on the protuberances and with a parallel arrangement near the edges on patterned surfaces.

Asymmetric Hydrogenation

K. Dong, Y. Li, Z. Wang,
K. Ding* ____________ **14191 – 14195**

Catalytic Asymmetric Hydrogenation of α-CF_3- or β-CF_3-Substituted Acrylic Acids using Rhodium(I) Complexes with a Combination of Chiral and Achiral Ligands

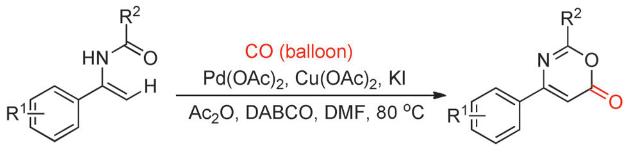


Only the mixture works! Acrylic acid derivatives with CF_3 substituents in α or β position were efficiently hydrogenated in the presence of a Rh^I complex with a chiral secondary phosphine oxide (SPO; see scheme) and an achiral Ph_3P as ligands. The corresponding propanoic acid derivatives were obtained with generally high conversion (> 99 %) and high enantioselectivity (92–> 99 %).

C–H Activation

M. Chen, Z.-H. Ren, Y.-Y. Wang,
Z.-H. Guan* ____________ **14196 – 14199**

Palladium-Catalyzed Oxidative Carbonylation of the Alkenyl C–H Bonds of Enamides: Synthesis of 1,3-Oxazin-6-ones

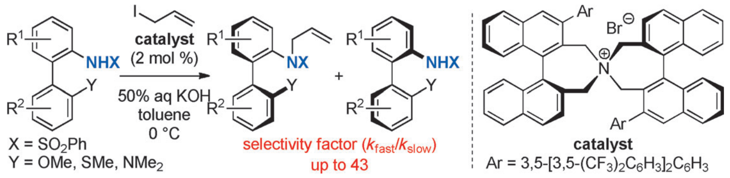


Palladium and CO.: The title reaction proceeds in the presence of CO, thus providing a synthesis for 1,3-oxazin-6-ones (see scheme; DABCO = 1,4-diazabicyclo[2.2.2]octane, DMF = *N*,*N*-dimethylformamide). The reaction tolerates a variety of functional groups on both the aryl ring and the amide of the substrate. Initial mechanistic studies suggest the activation of the alkenyl C–H bond to be a key step.

Asymmetric Synthesis

S. Shirakawa, X. Wu,
K. Maruoka* ____________ **14200 – 14203**

Kinetic Resolution of Axially Chiral 2-Amino-1,1′-Biaryls by Phase-Transfer-Catalyzed N-Allylation



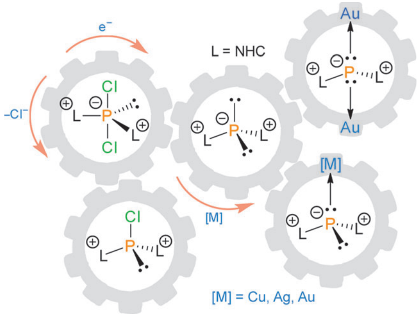
Going through a phase: The highly selective kinetic resolution of the title compounds, which are important chiral building blocks, was achieved by phase-transfer-catalyzed N-allylation. This synthetic method was applied to the highly enantioselective desymmetrization of a biaryl compound.

Coordination Chemistry

K. Schwedtmann, M. H. Holthausen,
K.-O. Feldmann,
J. J. Weigand* ____________ **14204 – 14208**

NHC-Mediated Synthesis of an Asymmetric, Cationic Phosphoranide, a Phosphanide, and Coinage-Metal Phosphanido Complexes

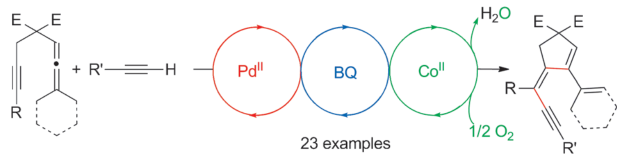
A cationic phosphoranide featuring a normal and an abnormal imidazoliumyl substituent was prepared through the reaction of a P-centered cation with an N-heterocyclic carbene (NHC). The remarkable reactivity of this compound allows the formation of two- or three-coordinate P-centered cations, illustrating the ability of imidazoliumyl substituents to stabilize high- and low-coordinated P atoms.



Homogeneous Catalysis

C. M. R. Volla,
J.-E. Bäckvall* ________ **14209 – 14213**

Palladium-Catalyzed Aerobic Domino Oxidative Carbocyclization-Alkynylation of Allenynes

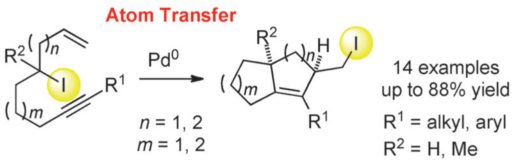


A breath of fresh air: Triene products with different R (H, aromatic or aliphatic) and R′ (aromatic and aliphatic) substituents (see scheme, BQ = benzoquinone) are formed selectively under aerobic conditions through the title reaction. Control experiments and kinetics provided valuable information about the reaction mechanism.

Atom Transfer

B. M. Monks, S. P. Cook* **14214 – 14218**

Palladium-Catalyzed Intramolecular Iodine-Transfer Reactions in the Presence of β-Hydrogen Atoms



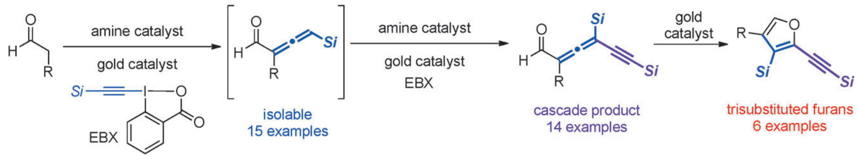
Atom economy: A palladium-catalyzed atom-transfer reaction of secondary alkyl iodides is described. An intramolecular double insertion of an alkyne and olefin provides access to primary iodides possessing β-hydrogen atoms. The process delivers these complex bicyclic homoallylic iodides with tetrasubstituted olefins from easily accessible aliphatic iodides. Different functional groups, including common heterocycles, are tolerated.

Synthetic Methods

Z. Wang, X. Li, Y. Huang* **14219 – 14223**

Direct α-Vinylidenation of Aldehydes and Subsequent Cascade: Gold and Amine Catalysts Work Synergistically

Inside Back Cover



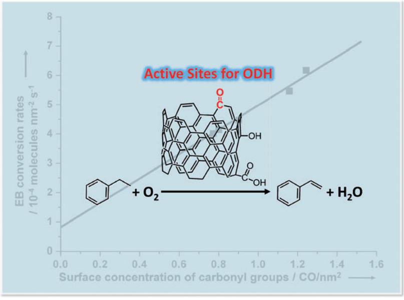
Gold and amine team up: Gold and an amine catalyst work synergistically to promote either an α-vinylidenation or an α-vinylidenation/γ-functionalization of aldehydes to generate tri- and tetrasubstituted allenes. The allene products also undergo an additional reaction to generate polysubstituted furans.

Heterogeneous Catalysis

W. Qi, W. Liu, B. Zhang, X. M. Gu,
X. L. Guo, D. S. Su* ____ **14224 – 14228**

Oxidative Dehydrogenation on Nanocarbon: Identification and Quantification of Active Sites by Chemical Titration

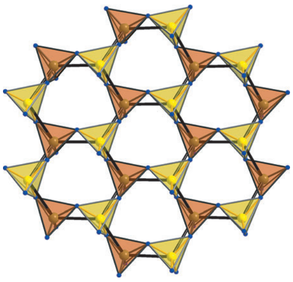
Ketonic carbonyl groups are catalytic active sites for oxidative dehydrogenation (ODH) reactions on carbon nanotubes. The quantity of these groups could be calculated from chemical titration with hydrazine compounds. ODH catalytic activity of nanocarbon is directly correlated with surface concentration of ketonic carbonyl groups, and the turnover frequency normalized by the number of active sites reflects the intrinsic activity of nanocarbon catalysts.



A Boron Sulfate

C. Logemann,
M. S. Wickleder* ———— **14229 – 14232**

$B_2S_2O_9$: A Boron Sulfate with Phyllosilicate Topology



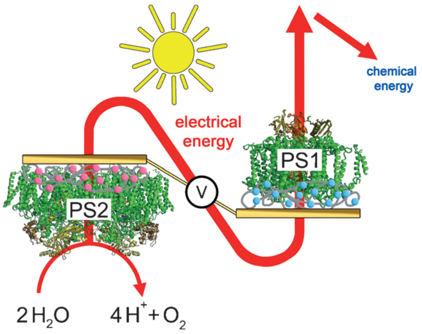
So many tetrahedra: The condensation of $[BO_4]$ (orange) and $[SO_4]$ (yellow) tetrahedra in the first binary boron sulfate $B_2S_2O_9$, leads to a structure with typical layered phyllosilicate topology. The compound is obtained from the hydrolysis of $B(OH)_3$ and HSO_3Cl.

Biophotovoltaics

T. Kothe, N. Plumeré, A. Badura,
M. M. Nowaczyk, D. A. Guschin,
M. Rögner,*
W. Schuhmann* ———— **14233 – 14236**

Combination of A Photosystem 1-Based Photocathode and a Photosystem 2-Based Photoanode to a Z-Scheme Mimic for Biophotovoltaic Applications

Z-Scheme on wires: The two photosystems of the natural photosynthetic Z-scheme have been connected by immobilizing them within redox hydrogels on individual electrodes. Upon irradiation, this biophotovoltaic device produced photocurrents as a closed and autonomous system. The open-circuit voltage of the cell corresponds to the potential difference between the two redox hydrogels and indicates the coupling of the two charge separation steps.

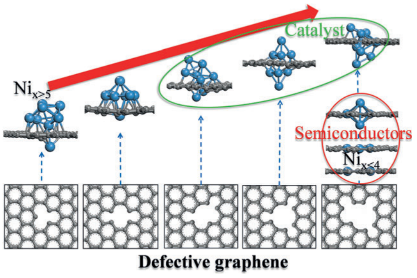


Graphene Functionalization

W. Gao, J. E. Mueller, J. Anton, Q. Jiang,
T. Jacob* ———— **14237 – 14241**

Nickel Cluster Growth on Defect Sites of Graphene: A Computational Study

Watching the defectives: DFT studies on the growth of nickel clusters on different graphene substrates shows that graphene defects essentially determine the morphology of the clusters. Defects greatly improve the catalytic reactivity of the larger clusters Ni_n ($5 \leq n \leq 10$). Smaller clusters Ni_n ($n < 4$) efficiently open the band gap of defective graphene, allowing a way to modulate the electronic properties of the graphene.

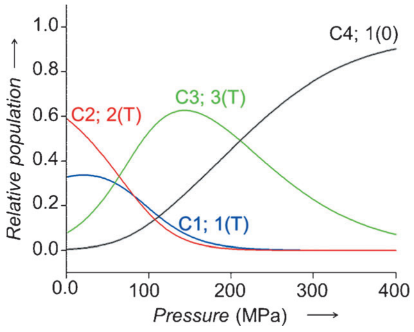


Intrinsic Allosteric Inhibition

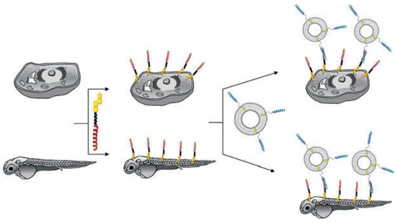
H. R. Kalbitzer,* I. C. Rosnizeck,
C. E. Munte, S. P. Narayanan, V. Kropf,
M. Spoerner ———— **14242 – 14246**

Intrinsic Allosteric Inhibition of Signaling Proteins by Targeting Rare Interaction States Detected by High-Pressure NMR Spectroscopy

A new type of allosteric inhibition by small molecules is proposed that should be applicable to all proteins involved intrinsically in protein–protein interactions. It is based on targeting their rare interaction states that can be detected by high-pressure NMR spectroscopy (see picture). An example is the Ras-protein where the protein–protein interaction of Ras with effectors can be modulated by small compounds that bind to the conformational states 1(T) or 1(0).



Superficial appeal: The surface of live cells and zebrafish embryos can be modified by a supramolecular method. A peptide pair that forms a coiled coil at the cell membrane can be used to dock liposomes in in vitro and in vivo environments (see scheme). This tool can be used in biophysical studies of biological processes occurring at membranes.



Functionalization of Biomembranes

H. R. Zope, F. Versluis, A. Ordas,
J. Voskuhl, H. P. Spaink,
A. Kros* ———— **14247 – 14251**

In Vitro and In Vivo Supramolecular Modification of Biomembranes Using a Lipidated Coiled-Coil Motif

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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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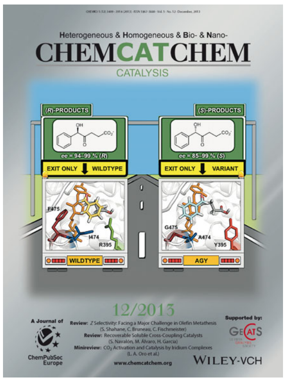

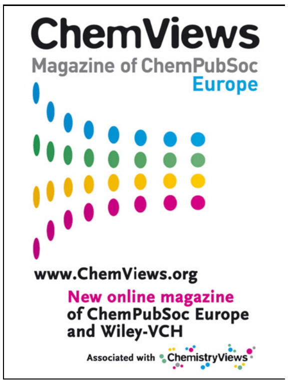

Abstracts for Communications

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In the abstract, the **motivation** for the work, the **methods** applied, the **results**, and the **conclusions** drawn should be presented (maximum 1000 characters). The abstract should contain several keywords to aid finding the paper online, and it should not mention graphical elements, tables, or references within the paper.