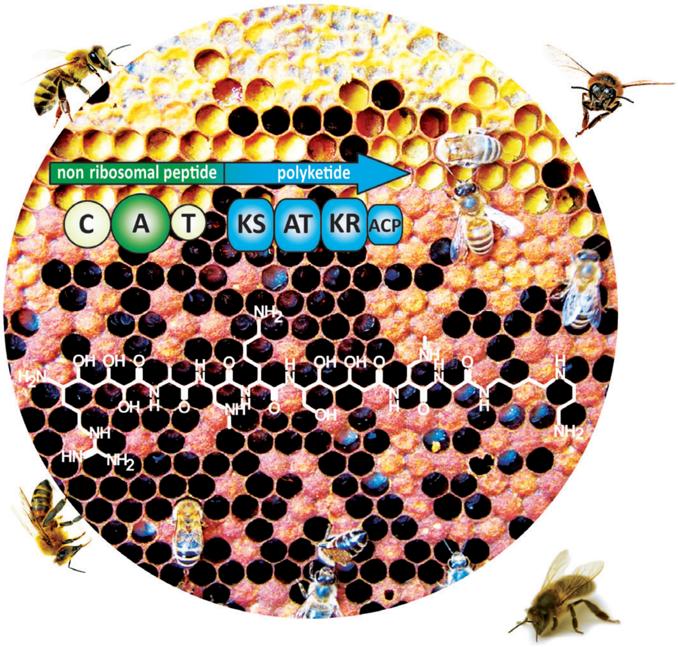
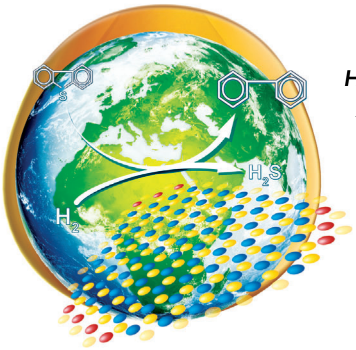
American Foulbrood ...



… is a widespread and devastating disease of the honey bee brood caused by the bacterium *Paenibacillus larvae*. In their Communication on page 10821 ff., R. D. Süssmuth et al. elucidated a fascinating nonribosomal biosynthesis through the isolation and structure elucidation of the antibacterial and antifungal paenilamicins. Furthermore, examination of the secondary metabolites of *P. larvae* sheds light on the virulence mechanisms.

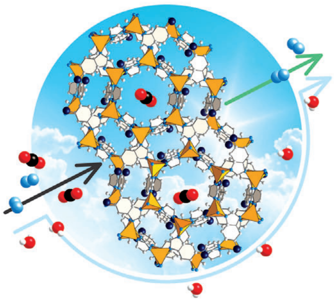
Protein Structures

Selecase reversibly commutes between four conformations of defined structure. F. X. Gomis-Rüth et al. report in their Communication on page 10624 ff. that the enzyme thus switches between competent and incompetent conformations for catalysis.



High-Resolution Microscopy

An industrial-style Co-Mo-S catalyst, which is typically used in hydrodesulfurization processes, was analyzed by S. Helveg et al. at the single-atom level by electron microscopy, as described in their Communication on page 10723 ff.



CO_2 Capture

O. M. Yaghi and co-workers show in their Communication on page 10645 ff. that even in the presence of water, hydrophobic zeolitic imidazolate frameworks (ZIFs) with the important chabazite topology can selectively capture CO_2.

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Service

Author Profile

"My own favorite saying is "There are 1000 ways of getting no signal".
I admire my co-workers ..."
This and more about Harald Schwalbe can be found on page 10576.

News

S. J. Miller

J. F. Hartwig

I. Hamachi

R. S. Langer

Obituaries

Bild: Thomas Knözinger

Professor Helmut Knözinger, an internationally leading scientist in catalysis and surface spectroscopy, died on Sunday January 14, 2014 in Munich. Knözinger developed the use of molecular probes to study catalytically active sites. He investigated a large number of catalytic reactions, with the goal of correlating the physicochemical characteristics of model catalysts with their catalytic properties in order to understand their function.

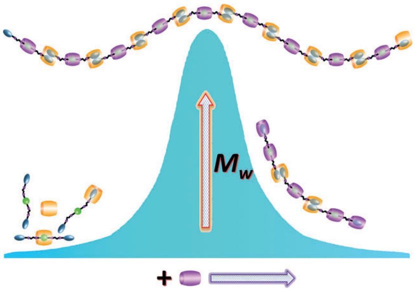
Highlights

Supramolecular Polymers

Q. Zhang, H. Tian* ______ **10582 – 10584**

Effective Integrative Supramolecular Polymerization

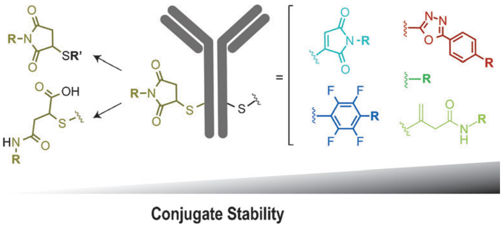
Exercise control: By taking advantage of self-sorting processes among host–guest components, a controlled supramolecular polymerization can be realized, as demonstrated recently with the preparation of a cucurbit[n]uril-based supramolecular polymer. This method may be used for the design of more ordered supramolecular polymers from complex and discrete components.



Protein Bioconjugation

P. M. S. D. Cal, G. J. L. Bernardes,*
P. M. P. Gois* ____________ **10585 – 10587**

Cysteine-Selective Reactions for Antibody Conjugation



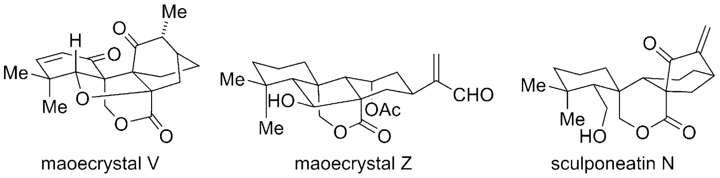
Moving tracks from maleimide: New site-selective protein modification reactions at cysteine have been developed. Unlike conventional maleimide conjugation, which results in a labile thioether succinimide, the new bioconjugation reactions result in stable conjugates and provide opportunities to develop a new generation of homogeneous, stable, and therapeutically useful conjugates.

Minireviews

Natural Product Synthesis

K. E. Lazarski, B. J. Moritz,
R. J. Thomson* ____________ **10588 – 10599**

The Total Synthesis of *Isodon* Diterpenes



An interesting family: Complex polycyclic diterpenes can be isolated from the plants of the *Isodon* genus. This Minireview gives a concise summary of recent synthetic efforts that have culminated in the successful total synthesis of these diterpenes.

For the USA and Canada:
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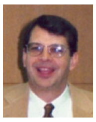
The Nagoya Medal of Organic Chemistry

The Nagoya Medal Prize was initially proposed by Professor Hisashi Yamamoto and Professor Ryoji Noyori, and founded in 1995 with Professor Noyori as the president through the financial support of Banyu Life Science Foundation International. The Nagoya Gold Medal Prize has been awarded every year to an Organic Chemist who has made significant original contributions to the field in its broadest sense. The first medal was presented to Professor Yoshito Kishi, and since then 23 eminent scientists have come to give lectures, including the Goto Memorial Lectureship started earlier. The Silver Medal, established in 1999, has been presented every year to a relatively younger Japanese scientist whose research has had a major impact on the field of synthetic organic chemistry. The medals are designed in the shape of a sword guard after an idea of Professors Yamamoto and Noyori. The flowers on the surface are lilies, which are the city flower of Nagoya City, and have the meaning of “a kind heart and competitiveness”. At their award lectures, recipients are asked to take enough time to talk not only about the profundity of their unique prize-winning chemistry but also the in-depth philosophy behind it, encouraging young chemists and students particularly in Nagoya region. In 2014, the Gold medal will be presented to **Professor John F. Hartwig**, and the Silver medal to **Professor Itaru Hamachi**.

Gold Medal Recipients

1995

Yoshito Kishi

1996

W. Clark Still

1997

Robert H. Grubbs

1998

Henri B. Kagan

1999

Samuel J. Danishefsky

2000

Manfred T. Reetz

2001

Kyriacos C. Nicolaou

2002

Dieter Seebach

2003

David A. Evans

2004

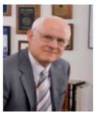
J. Fraser Stoddart

2005

Koji Nakanishi

2006

Steven V. Ley

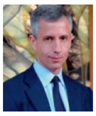
2007

Larry E. Overman

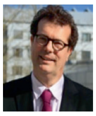
2008

Barry M. Trost

2009

Jean M. J. Fréchet

2011

Eric N. Jacobsen

2012

Paul Knochel

2013

Ben L. Feringa

2014

John F. Hartwig

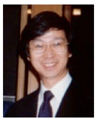
Silver Medal Recipients

1999

Keisuke Suzuki

2000

Takuzo Aida

2001

Eiichi Nakamura

2002

Shu Kobayashi

2003

Makoto Fujita

2004

Keiji Maruoka

2005

Michinori Suginome

2006

Jun-ichi Yoshida

2007

Mikiko Sodeoka

2008

Masahiro Murakami

2009

Kyoko Nozaki

2011

Keiji Tanino

2012

Takahiko Akiyama


Masahiro Terada

2013

Naoto Chatani

2014

Itaru Hamachi

Special Award


Her Royal Highness
Princess Chulabhorn Mahidol

2010 Anniversary Seminar


Ryoji Noyori, Hisashi Yamamoto
Silver Medalists

Goto Memorial Lectureship

1992

Derek Barton

1993

Albert Eschenmoser

1994

E. J. Corey

1995

Gilbert Stork

1997

Jean M. Lehn

1999

Yoshito Kishi

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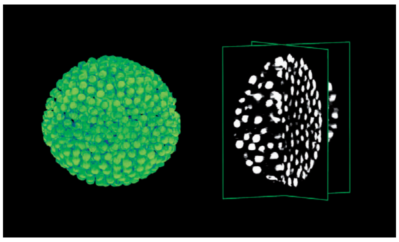
Reviews

Electron Tomography

S. Bals,* B. Goris, L. M. Liz-Marzán, G. Van Tendeloo ——— **10600 – 10610**

Three-Dimensional Characterization of Noble-Metal Nanoparticles and their Assemblies by Electron Tomography

A sight for small eyes: In 3D investigations of metal nanoparticles and their assemblies, electron tomography has become a versatile tool to understand the connection between the properties and structure or composition of nanomaterials. The different steps of an electron tomography experiment are discussed and how quantitative 3D information can be obtained even at the atomic scale is shown.

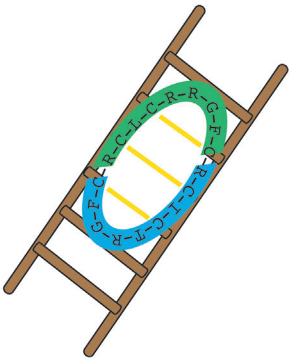


Theta Defensins

A. C. Conibear, D. J. Craik* ——— **10612 – 10623**

The Chemistry and Biology of Theta Defensins

Climbing up the ladder: Theta defensins are the only known cyclic backbone peptides from mammals and are characterized by the cyclic cystine ladder motif. They have promising applications as antimicrobials and peptide drug scaffolds, but little is known about their distribution in primate species or biosynthesis from two gene products. The Review discusses the progress in understanding the chemistry and biology of theta defensins and highlights remaining challenges and questions.



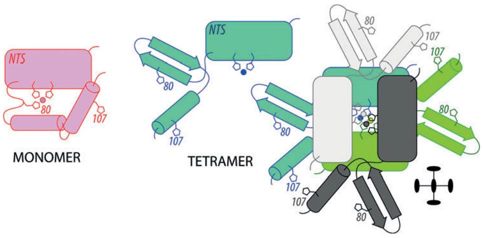
Communications

Enzymatic Activity

M. López-Pelegrín, N. Cerdà-Costa, A. Cintas-Pedrola, F. Herranz-Trillo, P. Bernadó, J. R. Peinado, J. L. Arolas, F. X. Gomis-Rüth* ——— **10624 – 10630**

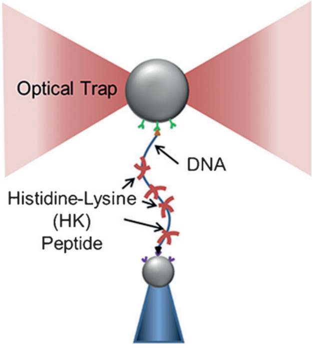
Multiple Stable Conformations Account for Reversible Concentration-Dependent Oligomerization and Autoinhibition of a Metamorphic Metallopeptidase

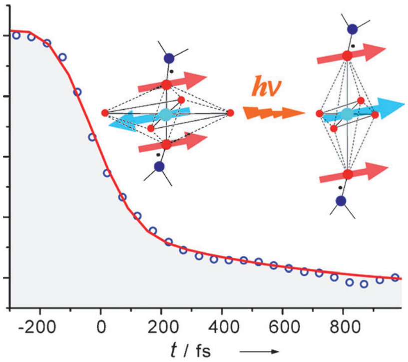
Frontispiece



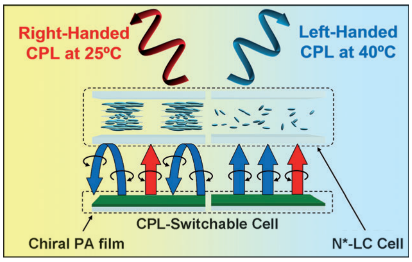
Shape shifting: A minimal metamorphic, selective, and specific caseinolytic metallopeptidase, selecase, reversibly transits between several different states of defined three-dimensional structure (monomer and tetramer represented in picture). The competent conformation is sequestered in incompetent but structured dimers, tetramers, and octamers, which are associated with loss of enzymatic activity due to autoinhibition.

Optical tweezers were used to directly measure single-molecule mechanical properties of DNA condensed using 19-mer poly-L-lysine (PLL) or branched histidine–lysine (HK) peptides. Force–extension profiles indicate that both carriers condense DNA actively. As the carrier concentration, pH, and the presence of zinc ions changes, DNA:HK complexes showed dynamically regulated mechanical properties at multiple force levels.

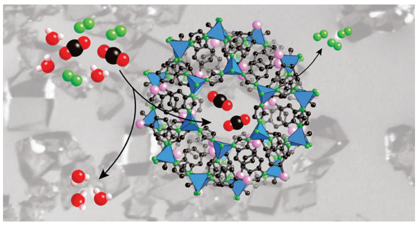




Almost instant: It takes less than 50 fs to switch the spin state of a copper-nitroxide-based molecular magnet using light. The timescale of the phenomenon and its mechanism have been investigated by using femtosecond optical spectroscopy. This type of photoswitching is promising for developing ultrafast photo-magnetic materials.



The circularly polarized luminescence (CPL) of chiral disubstituted liquid-crystalline polyacetylene (di-LCPA) was dynamically switched and amplified through the selective transmission of CPL across a thermotropic chiral nematic liquid crystal (N*-LC) phase. By combining a chiral di-LCPA CPL-emitting film with an N*-LC cell, a CPL-switchable cell was constructed.



Wetting their appetite for CO_2: Hydrophobic zeolitic imidazolate frameworks (ZIFs) with the chabazite (**CHA**) topology selectively capture CO_2 from N_2 in the presence of water. They thus overcome crucial challenges faced by many other porous materials for which even the smallest amount of water causes decomposition or decreases the materials' ability to capture CO_2.

Self-Assembly

W. Wu, A. M. Kirillov, X. Yan, P. Zhou,
W. Liu, Y. Tang* ________ **10649 – 10653**

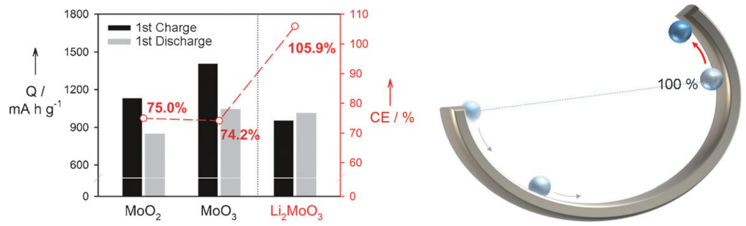
Enhanced Separation of Potassium Ions by Spontaneous K^+-Induced Self-Assembly of a Novel Metal–Organic Framework and Excess Specific Cation–π Interactions

A metal–organic framework (MOF) was fabricated by spontaneous K^+-induced supramolecular self-assembly with the embedded 3D ligand units supported by Fe_3O_4@mSiO_2 core-shell nanoparticles. The hybrid material based on Fe_3O_4@mSiO_2@MOF can selectively separate K^+ ions from a mixture of Na^+, K^+, Mg^{2+}, and Ca^{2+} ions, facilitated by a specific cation–π interaction between K^+ and the aromatic cavity of the MOF.

Lithium-Ion Batteries

J. Jang, Y. Kim, O. B. Chae, T. Yoon,
S.-M. Kim, H. S. Kim, H. Park, J. H. Ryu,
S. M. Oh* ____________ **10654 – 10657**

A First-Cycle Coulombic Efficiency Higher than 100 % Observed for a Li_2MO_3 (M = Mo or Ru) Electrode

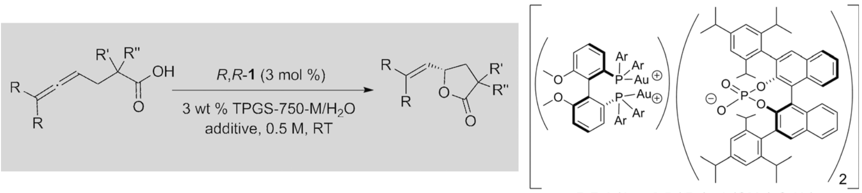


More out than in: Nano-sized metallic components (Mo or Ru), generated from Li_2MO_3 (M = Mo or Ru) by consuming four Li^+ ions and four electrons, react with Li_2O even just as a physical mixture. In the reaction with Li_2O the theoretical first-cycle Coulombic efficiency is 150 % because the metallic component is oxidized to MO_3 by the release of six Li^+ ions and six electrons per formula unit.

Micellar Catalysis

S. Handa, D. J. Lippincott, D. H. Aue,
B. H. Lipshutz* ________ **10658 – 10662**

Asymmetric Gold-Catalyzed Lactonizations in Water at Room Temperature



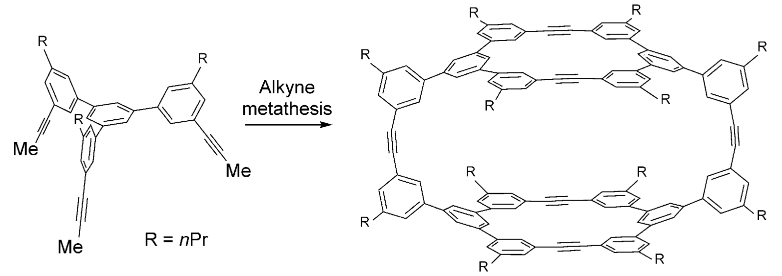
R,R-1 (Ar = 3,5-(tBu)$_2$-4-(OMe)-C$_6$H$_2$)

With tight quarters come more interactions! The high concentrations within nanomicelles can be used to force a close interaction between a nonracemic cationic metal complex and its nonracemic counterion, thereby maximizing the catalyst's impact on a given transformation. A chiral gold dicationic species and its associated phosphate anion are used to control absolute stereochemistry in newly formed γ-lactone products, derived from allenic carboxylic acids.

Alkyne Metathesis

Q. Wang, C. Zhang, B. C. Noll, H. Long,
Y. Jin, W. Zhang* ________ **10663 – 10667**

A Tetrameric Cage with D_{2h} Symmetry through Alkyne Metathesis

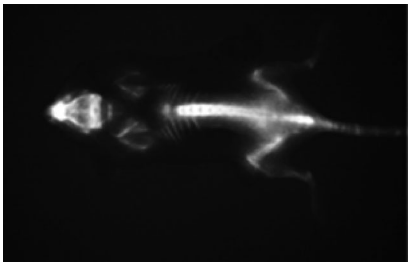


Clever cages: A tetrameric cage with a D_{2h} symmetry was prepared from a C_3-symmetric triyne monomer through a one-step alkyne metathesis. The tetramer consisting of two macrocyclic panels has a large internal cavity, which can selectively host C_{70} over C_{60}.

Contrast Agents

H. Hyun, H. Wada, K. Bao, J. Gravier, Y. Yadav, M. Laramie, M. Henary, J. V. Frangioni, H. S. Choi* ____ **10668 – 10672**

Phosphonated Near-Infrared Fluorophores for Biomedical Imaging of Bone

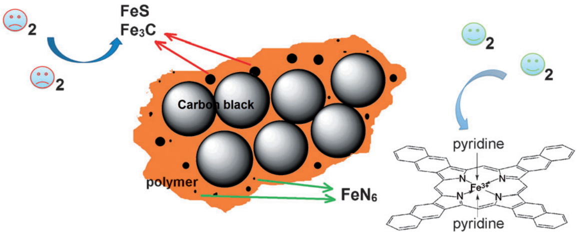


Bifunctional molecules with high-affinity binding to bone minerals as well as bright near-infrared fluorescence were obtained by attaching low-affinity pendant groups to the non-delocalized backbone of polymethines. These agents enable the non-invasive assessment of bone development over the course of weeks in living animals.

Fe/N/C Electrocatalysts for ORR

Y. S. Zhu, B. S. Zhang, X. Liu, D. W. Wang, D. S. Su* ____ **10673 – 10677**

Unravelling the Structure of Electrocatalytically Active Fe–N Complexes in Carbon for the Oxygen Reduction Reaction

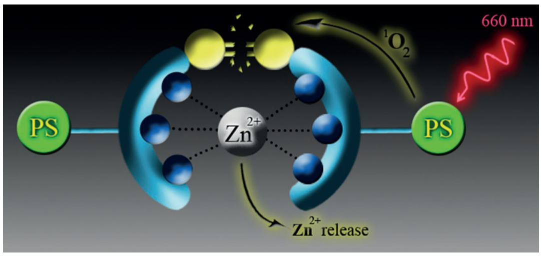


The active FeN$_x$ sites in Fe/N/C catalysts were identified by electron microscopy and Mössbauer spectroscopy as the six-coordinate Fe^{III} species [Fe^{III}(porphyrin)(pyridine)$_2$]. The results lead the way to target-specific synthesis of highly active and stable non-precious metal catalysts for oxygen reduction reaction.

Caged Compounds

A. Atilgan, E. Tanriverdi Eçik, R. Guliyev, T. B. Uyar, S. Erbas-Cakmak, E. U. Akkaya* ____ **10678 – 10681**

Near-IR-Triggered, Remote-Controlled Release of Metal Ions: A Novel Strategy for Caged Ions

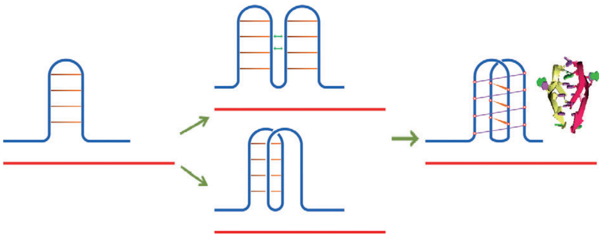


Metal ions on demand: Near-IR irradiation of a designer ligand results in singlet-oxygen-mediated fragmentation with the consequent release of metal ions. The modular nature of the “cage” may herald a new class of agents that could supply chemical effectors on demand.

DNA Structures

Y. W. Chen, C. R. Jhan, S. Neidle, M. H. Hou* ____ **10682 – 10686**

Structural Basis for the Identification of an i-Motif Tetraplex Core with a Parallel-Duplex Junction as a Structural Motif in CCG Triplet Repeats



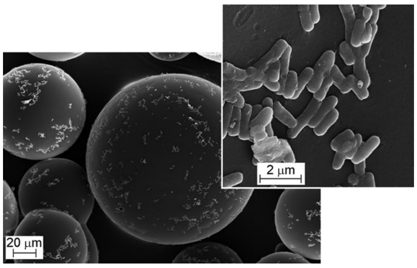
Too close for comfort: CCG-repeat DNA was found by X-ray crystallography to form a tetraplex combined with a parallel duplex, either by the association of hairpins or via a triplex intermediate (see picture). The observation of this i-motif structure suggests a possible molecular-level pathological consequence of CCG-triplet-repeat expansion with regard to neurological disease.

Bacterial Recognition

X. Shen, J. Svensson Bonde, T. Kamra,
L. Bülow, J. C. Leo, D. Linke,
L. Ye* ———— **10687 – 10690**

Bacterial Imprinting at Pickering
Emulsion Interfaces

Bacterial imprinting at interfaces: Using bacteria as both emulsion stabilizers and microbial templates, bacteria-imprinted sites are produced on polymer beads, which can facilitate microbial assembly on the surface. During the imprinting, the pre-polymers that match the target cell surface can be preferentially selected.

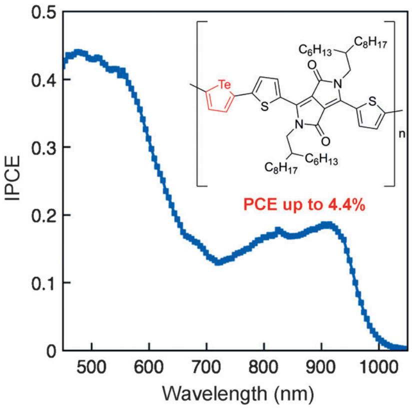


Organic Photovoltaics

Y. S. Park, Q. Wu, C.-Y. Nam,
R. B. Grubbs* ———— **10691 – 10695**

Polymerization of Tellurophene
Derivatives by Microwave-Assisted
Palladium-Catalyzed *ipso*-Arylative
Polymerization

Telluric rings: The tellurophene-containing low-bandgap polymer PDPPTe2T, prepared by microwave-assisted *ipso*-arylative polymerization, exhibited red-shifted absorption spectra compared to the thiophene analogue. Bulk heterojunction solar-cell devices from PDPPTe2T and $PC_{71}BM$ reach a power conversion efficiency of 4.4% and produce photocurrent at wavelengths up to 1 µm.

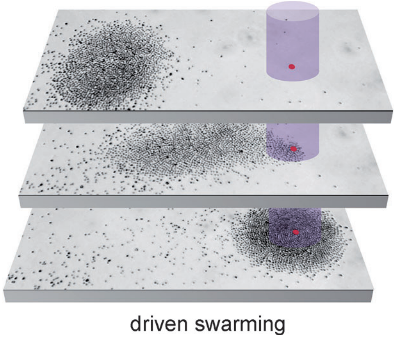


Colloidal Particles

S. Hernàndez-Navarro, P. Tierno,
J. A. Farrera, J. Ignés-Mullol,*
F. Sagués ———— **10696 – 10700**

Reconfigurable Swarms of Nematic
Colloids Controlled by Photoactivated
Surface Patterns

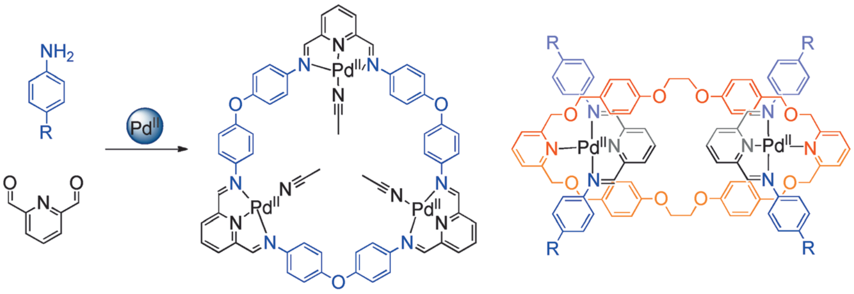
Swarming into focus: The assembly and transport of large ensembles of colloidal particles or droplets that are dispersed in a film of anisotropic fluid can be directly controlled by means of AC electrophoresis. Individual or collective particle steering is independently achieved by elastic modulation of the host nematic liquid crystal on a photosensitive confining surface.



Supramolecular Chemistry

C. Browne, T. K. Ronson,
J. R. Nitschke* ———— **10701 – 10705**

Palladium-Templated Subcomponent Self-Assembly of Macrocycles, Catenanes, and Rotaxanes

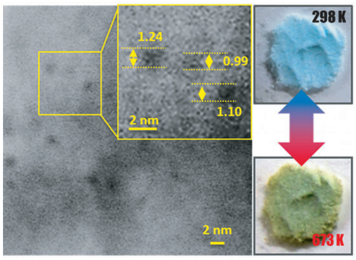


Mix and match: A range of different metallosupramolecular structures were obtained, including macrocycles (see picture) and host–guest systems, by combining Pd^{II} ions with 2,6-diformylpyridine and a variety of amines. Adding pyridine-based macrocyclic ligands allowed interlocked structures to be generated, such as rare examples of a doubly threaded [3]pseudorotaxane and [3]rotaxane.

Quantum Dots

H. Tamaki, H. Watanabe, S. Kamiyama,
Y. Oaki, H. Imai* ________ **10706 – 10709**

Size-Dependent Thermochromism through Enhanced Electron–Phonon Coupling in 1 nm Quantum Dots

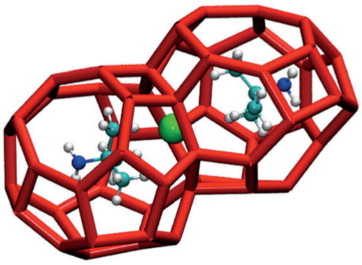


A dot matrix: 1 nm CuO quantum dots have been prepared in microporous silica. They exhibit unique and reversible color change from pale blue to deep green in a wide temperature range from 298 to 673 K. This thermochromism is ascribed to an enhanced bandgap shift that depends on temperature, with a strong electron–phonon coupling in the confined space of the 1 nm CuO quantum dots.

Inclusion Compounds

R. G. Grim, B. C. Barnes, P. G. Lafond,
W. A. Kockelmann, D. A. Keen, A. K. Soper,
M. Hiratsuka, K. Yasuoka, C. A. Koh,
A. K. Sum* ________ **10710 – 10713**

Observation of Interstitial Molecular Hydrogen in Clathrate Hydrates

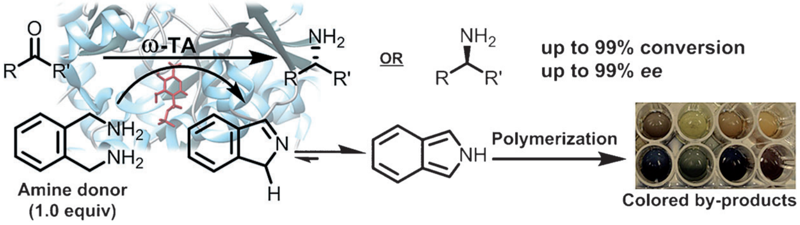


Breaking the boundaries: In the presence of molecular hydrogen, interstitial occupancy is observed in the type VI clathrate hydrate (see picture; *t*BuNH$_2$ in interstices (red) with H$_2$ (green)). This observation revises the definition of clathrate hydrate guest occupancy that assumes all guests are contained within the interior of the host water lattice.

Biocatalysis

A. P. Green,* N. J. Turner,*
E. O'Reilly* ________ **10714 – 10717**

Chiral Amine Synthesis Using ω-Transaminases: An Amine Donor that Displaces Equilibria and Enables High-Throughput Screening

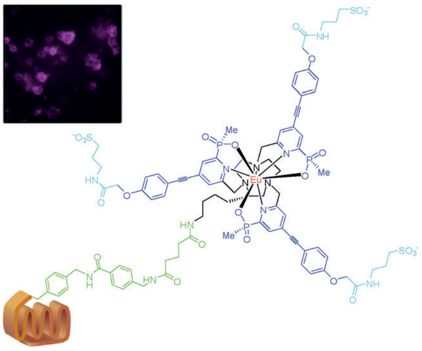


ω-Transaminases (ω-TA) have been employed as biocatalysts in a simple and efficient process for the synthesis of chiral amines. A dual-function diamine donor (*ortho*-xylylenediamine) serves to displace challenging reaction equilibria towards product formation whilst generating intensely colored by-products, which have allowed the development of liquid-phase and colony-based assays.

Lanthanides

M. Delbianco, V. Sadovnikova, E. Bourrier,
G. Mathis, L. Lamarque, J. M. Zwier,*
D. Parker* ________ **10718 – 10722**

Bright, Highly Water-Soluble Triazacyclononane Europium Complexes To Detect Ligand Binding with Time-Resolved FRET Microscopy

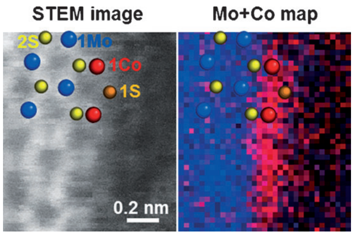


Bright and selective: Hydrophilic Eu^{III} complexes have been synthesized that suppress nonspecific binding and permit their use in bioconjugates using time-resolved assays, as exemplified for G protein-coupled receptor antagonists.

High-Resolution Microscopy

Y. Zhu, Q. M. Ramasse, M. Brorson, P. G. Moses, L. P. Hansen, C. F. Kisielowski, S. Helveg* ———— 10723 – 10727

Visualizing the Stoichiometry of Industrial-Style Co-Mo-S Catalysts with Single-Atom Sensitivity



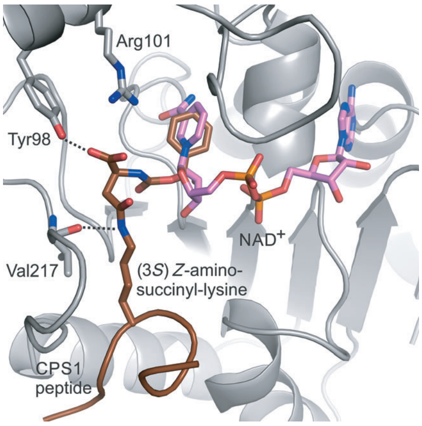
Promoting the edge: The structure of an industrial-style MoS_2 nanocatalyst with cobalt promoter atoms has been visualized using analytical electron microscopy with single-atom sensitivity. The stoichiometries of the catalytically important MoS_2 edge sites were unambiguously revealed atom by atom. These insights should facilitate the optimization of methods for the preparation of MoS_2 nanocatalysts.

Inside Back Cover

Enzymology

C. Roessler, T. Nowak, M. Pannek, M. Gertz, G. T. T. Nguyen, M. Scharfe, I. Born, W. Sippl, C. Steegborn, M. Schutkowski* ———— 10728 – 10732

Chemical Probing of the Human Sirtuin 5 Active Site Reveals Its Substrate Acyl Specificity and Peptide-Based Inhibitors

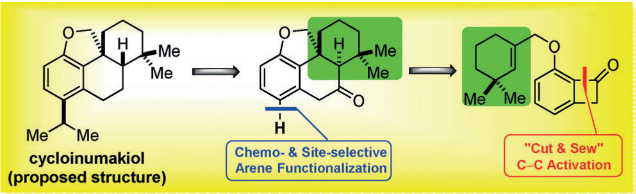


Small changes make the difference: Systematic investigation of the acyl substrate specificity of sitruin 5 uncovers its unique preference for succinyl and glutaryl residues. Depending on the chemical nature of introduced modifications, either high-affinity substrates or sirtuin 5 specific inhibitors could be obtained.

Natural Product Synthesis

T. Xu, G. Dong* ———— 10733 – 10736

Coupling of Sterically Hindered Trisubstituted Olefins and Benzocyclobutenones by C–C Activation: Total Synthesis and Structural Revision of Cycloinumakiol

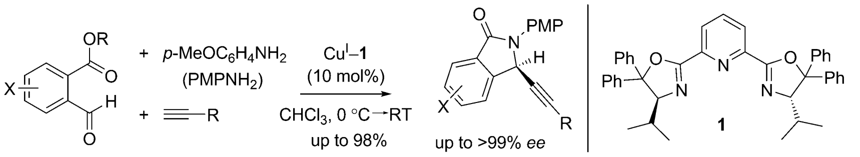


The mystery is solved: The first total synthesis of the proposed structure of cycloinumakiol has been achieved by rhodium catalysis. In the key step, the coupling of a trisubstituted olefin with a benzocyclobutenone through C–C activation yields the tetracyclic core skeleton. Comparison of the synthetic product to natural cycloinumakiol revealed a misassignment, and the natural compound was unambiguously identified as 19-hydroxytotarol.

Asymmetric Catalysis

V. Bisai, A. Suneja,
V. K. Singh* ________ **10737 – 10741**

Asymmetric Alkynylation/Lactamization Cascade: An Expeditious Entry to Enantiomerically Enriched Isoindolinones



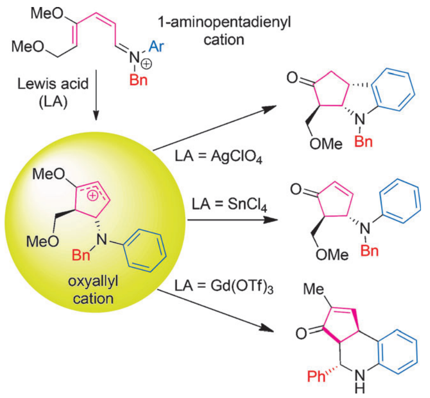
Simple and effective: A highly enantioselective domino alkynylation/lactamization involving the formation of one C–C and two C–N bonds was developed for the synthesis of diversely substituted isoindolinones (see scheme). The methodology was further extended to the synthesis of tetrahydroisoquinoline scaffolds found in a variety of biologically active natural products by a remarkably selective two-step procedure (up to 94 % *ee*).

Cyclizations

R. William, S. Wang, F. Ding,
E. N. Arviana, X.-W. Liu* _ **10742 – 10746**

Interrupted Imino-Nazarov Cyclization of 1-Aminopentadienyl Cation and Related Cascade Process

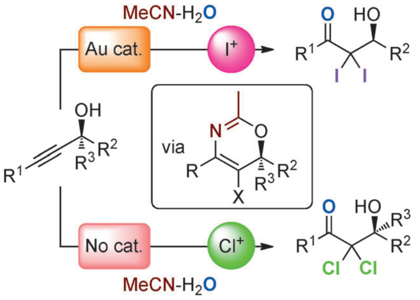
Taking control: The fate of an oxyallyl cation formed through a 4π conrotatory imino-Nazarov cyclization can be controlled to access cyclopentanoid frameworks. In the presence of silver(I), intramolecular arene trapping leads to indoline-fused cyclopentanones. Gadolinium(III) facilitates a cascade transformation to furnish tetrahydroquinoline-fused cyclopentenones. Tf = trifluoromethanesulfonyl.



Halogenation

J. M. D'Oyley, A. E. Aliev,
T. D. Sheppard* ________ **10747 – 10750**

Regioselective Dihalohydration Reactions of Propargylic Alcohols: Gold-Catalyzed and Noncatalyzed Reactions



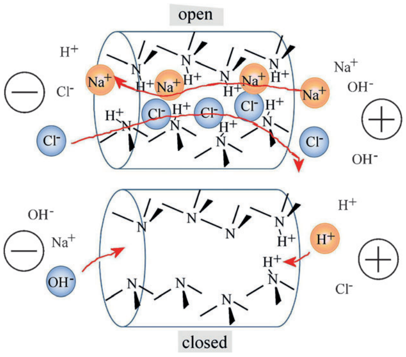
With or without gold: Propargylic alcohols were converted into α,α-diiodo-β-hydroxyketones by treatment with *N*-iodosuccinimide in the presence of a gold catalyst. α,α-Dichloro-β-hydroxyketones were prepared without a catalyst by reaction of propargylic alcohols with trichloroisocyanuric acid. Mechanistic studies suggest that both of these reactions proceed via the formation of 5-halooxazines, formed by participation of the acetonitrile solvent.

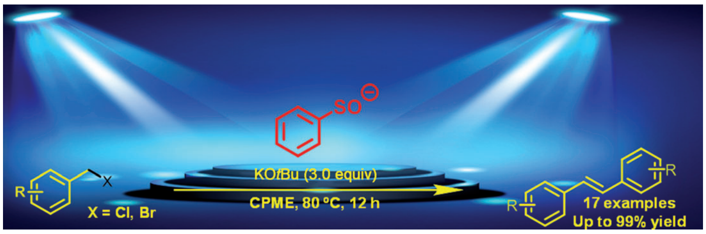
Ionic Diodes

E. Madrid, Y. Rong, M. Carta,
N. B. McKeown,* R. Malpass-Evans,
G. A. Attard, T. J. Clarke, S. H. Taylor,
Y.-T. Long, F. Marken* __ **10751 – 10754**

Metastable Ionic Diodes Derived from an Amine-Based Polymer of Intrinsic Microporosity

Ionic flip-flop: Polymers with intrinsic microporosity introduce ionic diode and metastable switching effects as a result of their rigid backbone and molecular-structure-dependent anion versus cation conductivity.



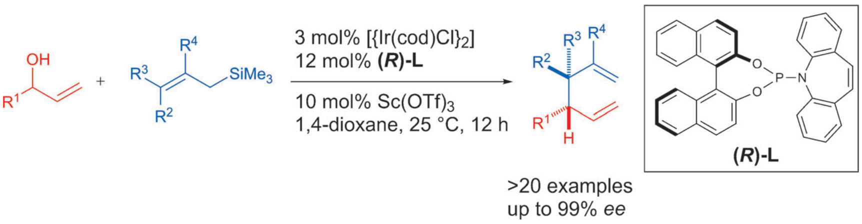


Sulfenates take center stage: Sulfenate anions are known as highly reactive species in the organic arena. Now they premiere as organocatalysts: A sulfoxide/sulfenate (1–10 mol %) promotes the transformation of benzyl halides into *trans*-stilbenes under basic conditions (up to 99 % yield). CPME = cyclopentyl methyl ether.

Organocatalysis

M. Zhang, T. Jia, H. Yin, P. J. Carroll,
E. J. Schelter, P. J. Walsh* **10755 – 10758**

A New Class of Organocatalysts: Sulfenate Anions



Enantioselective allyl–allylsilane cross-coupling between branched racemic allylic alcohols and allylsilanes was developed. An Ir-(P,olefin) catalyst in conjunction with Sc(OTf)$_3$ as the acidic promoter enables the preparation of chiral 1,5-dienes with up to 99 % *ee*. The described method was successfully applied to the asymmetric synthesis of the pyrethroid insecticide protrifenbute. cod = 1,5-cyclooctadiene, Tf = trifluoromethanesulfonyl.

Asymmetric Catalysis

J. Y. Hamilton, N. Hauser, D. Sarlah,
E. M. Carreira* ________ **10759 – 10762**

Iridium-Catalyzed Enantioselective Allyl–Allylsilane Cross-Coupling

up to 99% yield, 20:1 d.r., 99% *ee*

Square deal: A combination of either ruthenium(II) or rhodium(II) complexes and quinine-derived squaramide enables 3-diazooxindoles, indole, and nitroalkenes to undergo a highly efficient asymmetric three-component reaction. Based on this metal/organo relay catalysis, a total synthesis of (−)-folicanthine was accomplished in seven steps with 14.5 % overall yield.

Carbenoids

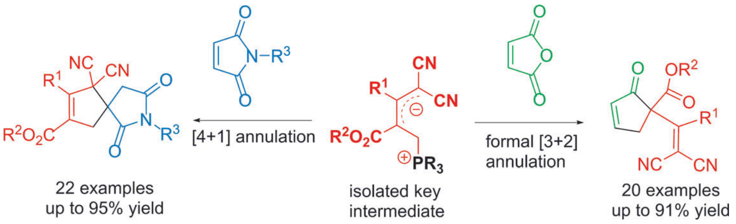
D.-F. Chen, F. Zhao, Y. Hu,
L.-Z. Gong* ________ **10763 – 10767**

C–H Functionalization/Asymmetric Michael Addition Cascade Enabled by Relay Catalysis: Metal Carbenoid Used for C–C Bond Formation

Organocatalysis

X.-N. Zhang, G.-Q. Chen, X.-Y. Tang, Y. Wei, M. Shi* ______ **10768 – 10773**

Phosphine-Catalyzed Annulations of 4,4-Dicyano-2-Methylenebut-3-enoates with Maleimides and Maleic Anhydride

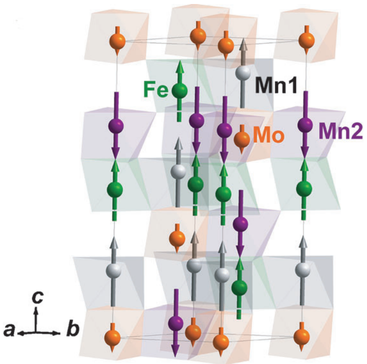


Formalities: Novel phosphine-catalyzed [4+1] and formal [3+2] annulations of 4,4-dicyano-2-methylenebut-3-enoates with maleimides and maleic anhydride, respectively, have been developed. Maleimides served as C_1 synthons and maleic anhydride behaved as a C_3 synthon to afford the corresponding compounds. A phosphinium-containing zwitterion is the key intermediate in both annulations.

Polar Magnet

M. R. Li, M. Retuerto, D. Walker, T. Sarkar, P. W. Stephens, S. Mukherjee, T. S. Dasgupta, J. P. Hodges, M. Croft, C. P. Grams, J. Hemberger, J. Sánchez-Benítez, A. Huq, F. O. Saouma, J. I. Jang, M. Greenblatt* **10774 – 10778**

Magnetic-Structure-Stabilized Polarization in an Above-Room-Temperature Ferrimagnet

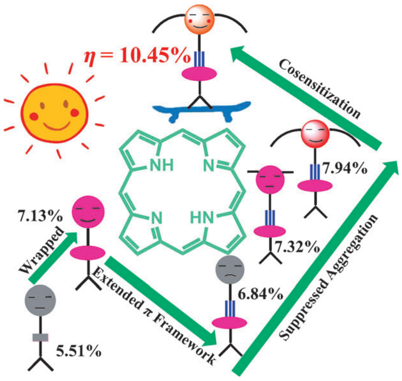


Magnetoelectric materials: Polar and ferrimagnetic Mn_2FeMoO_6 ($T_C = 337$ K) adopts the non-centrosymmetric Ni_3TeO_6-type ($R3$) structure confirmed by the second harmonic generation. DFT calculations indicate spontaneous polarization of 68 $\mu C\,cm^{-2}$ and demonstrate that its structural polarization, which breaks the polarization rule in perovskites and related phases, is energetically stabilized by the magnetic structure based on the Ni_3TeO_6 prototype.

Solar Cells

Y. Q. Wang, B. Chen, W. J. Wu, X. Li, W. H. Zhu, H. Tian, Y. S. Xie* ______ **10779 – 10783**

Efficient Solar Cells Sensitized by Porphyrins with an Extended Conjugation Framework and a Carbazole Donor: From Molecular Design to Cosensitization

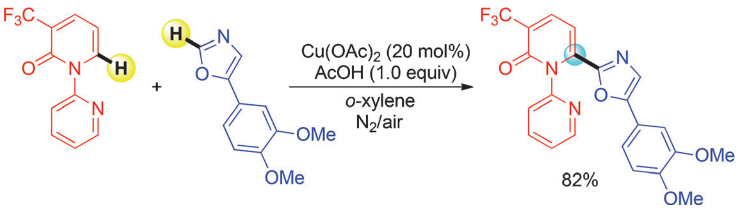


All wrapped up: Porphyrin dyes containing the carbazole electron donor have been designed and optimized by wrapping the porphyrin framework, using an ethynylene bridge, and aggregation suppression by introducing additional alkoxy chains. Using a cosensitizer, the highest cell efficiency of 10.45 % is achieved. This work provides an effective combined strategy of molecular design and cosensitization for developing efficient DSSCs.

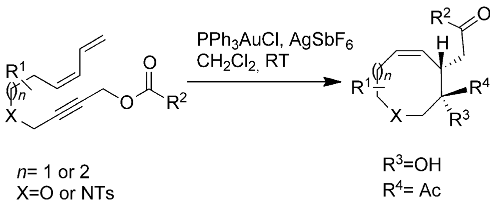
Synthetic Methods

R. Odani, K. Hirano,* T. Satoh, M. Miura* ______ **10784 – 10788**

Copper-Mediated C6-Selective Dehydrogenative Heteroarylation of 2-Pyridones with 1,3-Azoles



Appointment of a temporary director: A copper-mediated C6-selective dehydrogenative arylation of 2-pyridones with 1,3-azoles was developed with the aid of an attachable/detachable pyridine-based directing group (see scheme). The reaction proceeded effectively without a noble metal, and in some cases molecular oxygen in air rendered the process catalytic in copper.



Happy medium: A highly efficient strategy for the synthesis of the title compounds has been developed. This transformation successfully demonstrates the power of a gold-catalyzed cycloaddition reaction to prepare various functionalized medium-sized rings. This method also represents one of the few transition-metal-catalyzed intramolecular cycloaddition reactions for the synthesis of medium-sized rings. Ts = 4-toluenesulfonyl.

Synthetic Methods

C. Zhao, X. Xie, S. Duan, H. Li, R. Fang, X. She* ________ **10789 – 10793**

Gold-Catalyzed 1,2-Acyloxy Migration/Intramolecular [3+2] 1,3-Dipolar Cycloaddtion Cascade Reaction: An Efficient Strategy for Syntheses of Medium-Sized-Ring Ethers and Amines

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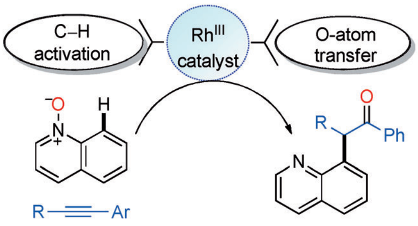
A chance meeting: A rhodium(III)-catalyzed redox-neutral coupling of quinoline *N*-oxides with alkynes has been realized, thus leading to the synthesis of α-substituted acetophenones. This system integrates C–H activation with O-atom transfer.



C–H Activation

X. Zhang, Z. Qi, X. Li* ____ **10794 – 10798**

Rhodium(III)-Catalyzed C–C and C–O Coupling of Quinoline *N*-Oxides with Alkynes: Combination of C–H Activation with O-Atom Transfer

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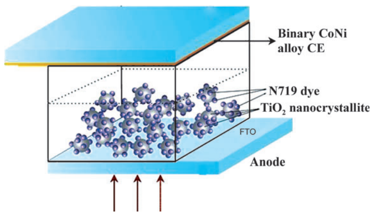

A mild hydrothermal reduction strategy has been used to generate Pt-free binary Co-Ni alloys for use as counter electrode (CE) materials in dye-sensitized solar cells (DSSCs). These materials offer high electrocatalytic activity toward I_3^-, good electron conduction, as well as cost-effectiveness. A conversion efficiency of 8.39 % was measured under one sun irradiation, which is much higher than the 6.96 % from platinum-based DSSCs.

Energy Conversion

X. Chen, Q. Tang,* B. He, L. Lin, L. Yu* ________ **10799 – 10803**

Platinum-Free Binary Co-Ni Alloy Counter Electrodes for Efficient Dye-Sensitized Solar Cells

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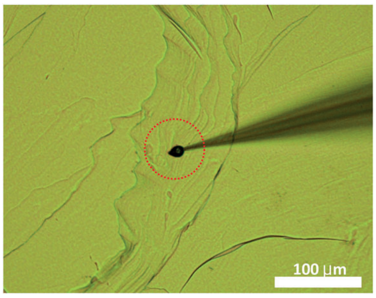
On the cutting edge: To study the oxygen reduction reaction (ORR), an air-saturated electrolyte solution droplet with a diameter of approximately 15 μm was deposited at a specified position on the edge (see picture) or on the basal plane of highly oriented pyrolytic graphite. Electrochemical measurements suggest that the edge sites are catalytically more active than basal-plane sites towards the ORR.



Oxygen Reduction Reaction

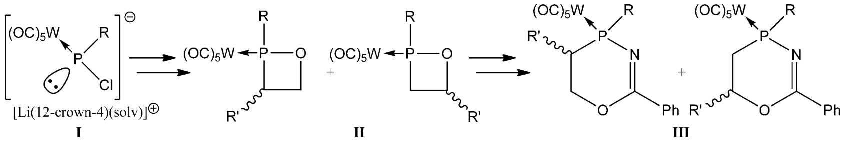
A. Shen, Y. Zou, Q. Wang, R. A. W. Dryfe, X. Huang, S. Dou, L. Dai,* S. Wang* ________ **10804 – 10808**

Oxygen Reduction Reaction in a Droplet on Graphite: Direct Evidence that the Edge Is More Active than the Basal Plane

1,2-Oxaphosphetane Complexes

A. W. Kyri, V. Nesterov, G. Schnakenburg, R. Streubel* ———— 10809 – 10812

Synthesis and Reaction of the First 1,2-Oxaphosphetane Complexes

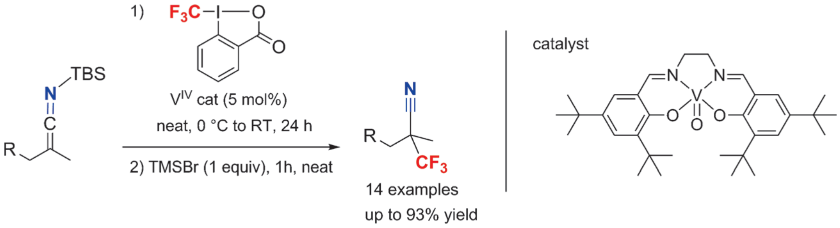


O-P^{III}eration successful: The first 1,2-oxaphosphetane complexes **II** were synthesized by a formal P$_1$ insertion into the C–O bond of different epoxides using the Li/Cl phosphinidenoid complex **I** (see scheme; R = CH(SiMe$_3$)$_2$, solv = solvent). The reaction of a mixture of **II** and trifluoromethane sulfonic acid/benzonitrile/triethylamine led to a ring-expansion formation of the 1,3,4-oxazaphosphacyclohex-2-ene complex **III**.

Trifluoromethylation

N. Früh, A. Togni* ———— 10813 – 10816

Vanadium-Catalyzed Solvent-Free Synthesis of Quaternary α-Trifluoromethyl Nitriles by Electrophilic Trifluoromethylation



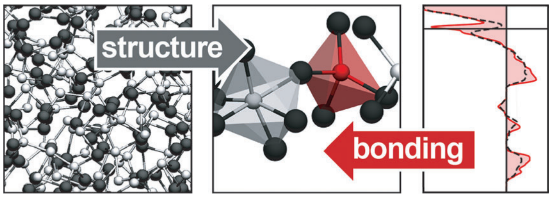
Not only copper! Oxovanadium(IV) complexes catalyze the trifluoromethylation of silyl ketene imines with hypervalent iodine reagents to form quaternary α-trifluoromethyl nitriles under solvent-free conditions. The products, formed in up to 93% yield, may be further transformed into useful synthetic building blocks for organofluorine chemistry.

Amorphous Materials

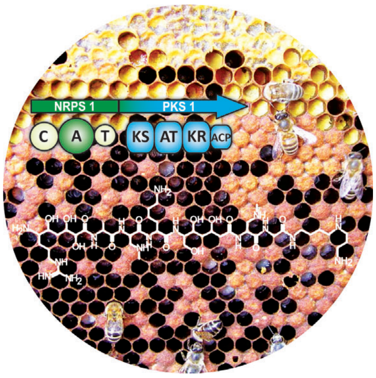
V. L. Deringer, W. Zhang, M. Lumeij, S. Maintz, M. Wuttig, R. Mazzarello,* R. Dronskowski* ———— 10817 – 10820

Bonding Nature of Local Structural Motifs in Amorphous GeTe

Inside Cover



Amorphous—no problem! Analyzing a crystalline structure by breaking it down into local fragments and covalent bonds is a technique that chemists have long perfected. With new tools at hand, this chemical language can be extended to amorphous solid-state materials—in this case, to the phase-change memory alloy germanium telluride.



The bee all and end all? American Foulbrood, which is caused by the bacterium *Paenibacillus larvae,* is a widespread and devastating disease of the honey bee brood. Through the isolation and structure elucidation of the antibacterial and antifungal paenilamicins, a fascinating nonribosomal biosynthesis has been deciphered. The study of the secondary metabolites of *P. larvae* sheds light on the virulence mechanisms of this serious disease.

Natural Products

S. Müller, E. Garcia-Gonzalez, A. Mainz,
G. Hertlein, N. C. Heid, E. Mösker,
H. van den Elst, H. S. Overkleeft,
E. Genersch,
R. D. Süssmuth* ______ **10821 – 10825**

Paenilamicin: Structure and Biosynthesis of a Hybrid Nonribosomal Peptide/Polyketide Antibiotic from the Bee Pathogen *Paenibacillus larvae*

Front Cover

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

Angewandte Corrigendum

Distillable Ionic Liquids: Reversible Amide O Alkylation

Z.-J. Chen, H.-W. Xi, K. H. Lim,
J.-M. Lee* ______ **13392–13396**

Angew. Chem. Int. Ed. **2013**, *52*

DOI: 10.1002/anie.201306476

In this Communication, some important early references were not included. Herein, references [15b–h] are reviewed, and the fifth to seventh sentences in the second paragraph on page 13392 are rewritten as follows:

"Recently, low-cost amide cation-based ILs were developed and applied in liquid crystals,[12] electrolytes,[13] solvent extraction of metal ions,[14] ionothermal carbonization of sugars,[15a] and more. In amides, there are two possible alkylation sites: the amide nitrogen and carbonyl oxygen. Though the O-alkylation mechanism for amides was already proposed in 1956,[15b] and later adopted elsewhere,[13d, 14, 15a,c–h] N-alkylation mechanism was still in use until recently.[12, 13a–c] In 1961, H. Bredereck et al.[15d,e] reported that the O-alkylation of *N*,*N*-dimethylformamide with dimethylsulfate is reversible with temperature, and the complex is distillable at the temperatures, above 110 °C."

The authors would like to acknowledge Prof. Willi Kantlehner for the suggestion of the references.

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