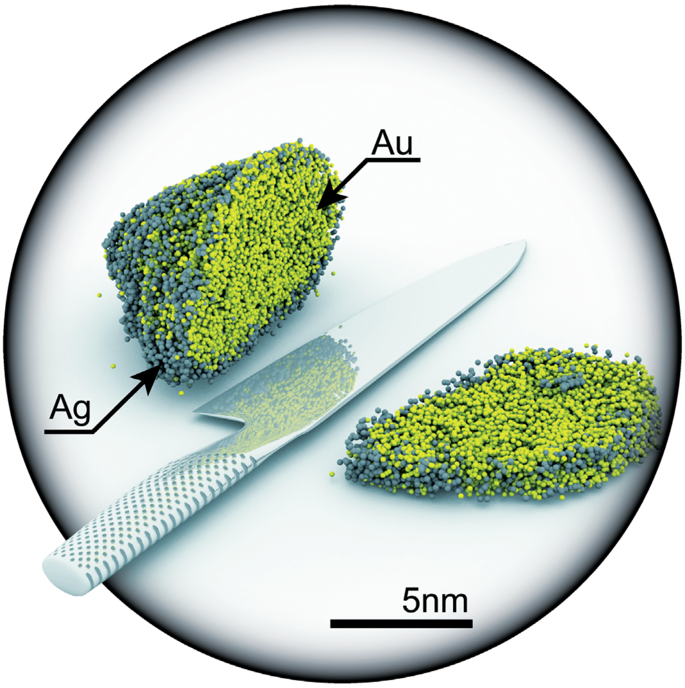
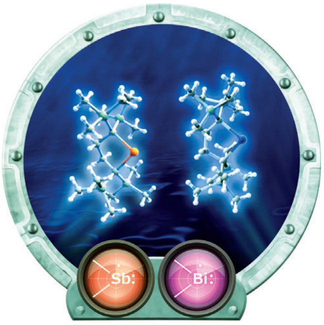
Slice by slice …

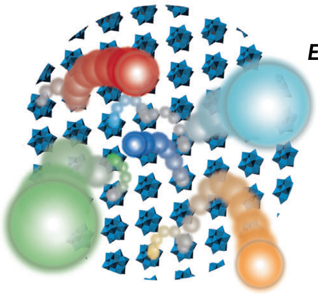


… atom probe tomography data from a Au@Ag core–shell nanoparticle reveals the arrangement of the atoms throughout the particle. The Cover Picture shows the distribution of Au (yellow) and Ag (gray) atoms within a 15 nm nanoparticle, determined with near-atomic resolution by T. Maschmeyer and co-workers in their Communication on page 11190 ff. The elements are not evenly distributed across the surface, a result of surface morphology and of residues from the particle synthesis.

Persistent Sb and Bi Radicals

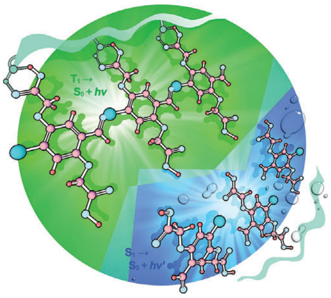
Synthesis and spectroscopic characterization of persistent stibinyl and bismuthinyl radicals in solution is described by S. Ishida, T. Iwamoto et al. in their Communication on page 11172 ff.





Electron Transport

By linking polyoxometalate clusters together with π-molecule wires R. Tsunashima et al. show in their Communication on page 11128 ff. that electron-transport can occur between the clusters by electron hopping.



Phosphorescence

J. Kim and co-workers show in their Communication on page 11177 ff. that modulation of the strength of halogen and hydrogen bonding in an organic phosphor–poly(vinyl alcohol) system by water enables reversible switching between phosphorescence and fluorescence.

How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

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Editorial

"... Molecules, of which the catenanes and rotaxanes are the archetypal examples, with mechanical bonds have emerged during their 50-year lifespan with ever-increasing frequency—after an induction period that lasted almost two decades—from being little more than intellectual curiosities to becoming one of the cornerstones of molecular nanotechnology ..."
Read more in the Editorial by J. Fraser Stoddart.

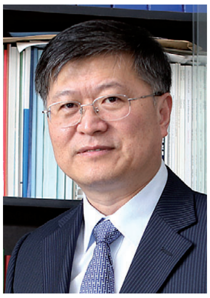
J. F. Stoddart* ———— **11102–11104**

Putting Mechanically Interlocked Molecules (MIMs) to Work in Tomorrow's World

Service

Spotlight on Angewandte's Sister Journals **11121–11123**

Author Profile



"My worst nightmare is falling off a high mountain. I lose track of time when I read my favorite fiction books. ..."
This and more about He Tian can be found on page 11128.

He Tian ———— **11128**

News

W. Leitner

J. Klankermayer

T. F. Hofmann

F. Diederich

European Sustainable Chemistry Award:
W. Leitner and J. Klankermayer ——— **11129**

Advancement of the Application of Agricultural and Food Chemistry Award: T. F. Hofmann ———— **11129**

Bohlmann Lectureship:
F. Diederich ———— **11129**

Books

Intelligent Stimuli-Responsive Materials Quan Li *reviewed by A. P. H. J. Schenning* — **11130**

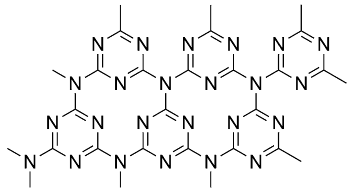
Highlights

Carbon(IV) Nitrides

E. Kroke* — **11134 – 11136**

gt-C_3N_4—The First Stable Binary Carbon(IV) Nitride

Twenty-five years ago a diamondlike C_3N_4 phase was postulated. After many unsuccessful attempts the synthesis of an s-triazine-based modification was accomplished, which is reported to show interesting semiconducting and catalytic properties similar to that of graphene and related graphitic C/N/H phases.

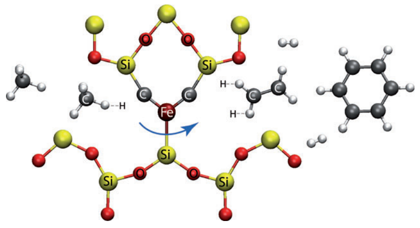


Heterogeneous Catalysis

M. Ruitenbeek,*
B. M. Weckhuysen* — **11137 – 11139**

A Radical Twist to the Versatile Behavior of Iron in Selective Methane Activation

Things go better without coke! The selective activation of methane and its direct conversion into light olefins and aromatic compounds remains a formidable challenge. Recent work shows that a catalyst material consisting of lattice-confined single iron atoms is very active and selective in the direct, nonoxidative conversion of methane into ethylene, benzene, and naphthalene without the formation of coke deposits.

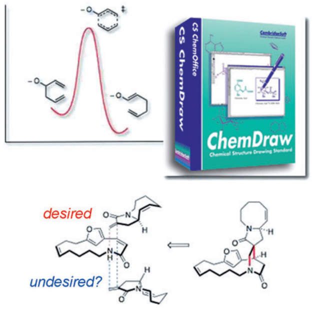


Essays

Development of ChemDraw

D. A. Evans* — **11140 – 11145**

History of the Harvard ChemDraw Project



Remember when…? This Essay describes the collaboration between Stewart Rubenstein and David and Sally Evans to develop the chemical graphics program ChemDraw, which was introduced in 1986. Now, three decades later, this software has become the dominant vehicle for drawing chemical structures in the organic chemistry community.

For the USA and Canada:
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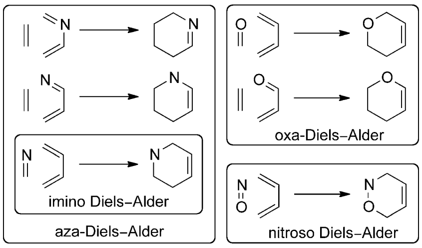
Minireviews

Asymmetric Synthesis

V. Eschenbrenner-Lux, K. Kumar,*
H. Waldmann* ________ **11146 – 11157**

The Asymmetric Hetero-Diels–Alder Reaction in the Syntheses of Biologically Relevant Compounds



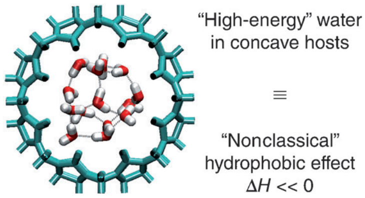
The right tools: The hetero-Diels–Alder reaction is a powerful method for constructing six-membered aza- and oxa-ring systems. This Minireview provides an overview of the application of this reaction in the synthesis of natural products and other biologically relevant small molecules.

Reviews

Hydrophobic Effect

F. Biedermann,* W. M. Nau,*
H.-J. Schneider* ________ **11158 – 11171**

The Hydrophobic Effect Revisited—Studies with Supramolecular Complexes Imply High-Energy Water as a Noncovalent Driving Force



Overcoming a phobia: Hydrophobic effects are traditionally described by the association of two lipophilic molecules, which then need less water molecules for solvation than two separate solutes, thus leading to either entropy or enthalpy gain. Investigations with supramolecular complexes have shown that another mechanism based on the replacement of hydrogen-bond-deficient high-energy water molecules in cavities can play a decisive role.

Communications

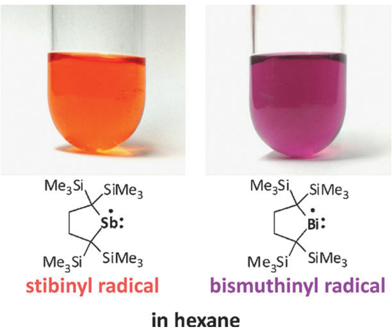
Radicals

S. Ishida,* F. Hirakawa, K. Furukawa,
K. Yoza, T. Iwamoto* ____ **11172 – 11176**

Persistent Antimony- and Bismuth-Centered Radicals in Solution

Frontispiece

Persistent: The facile dissociation of distibines and dibismuthines with bulky bidentate alkyl groups leads to the corresponding persistent radicals in solution. The stibinyl and bismuthinyl radicals were spectroscopically characterized, and the thermodynamic parameters for their dissociation equilibria were estimated. The radicals reacted with a stable nitroxyl radical to give the cross-radical coupling products in good yields.

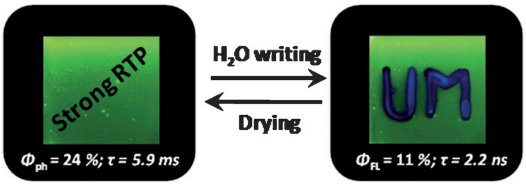


Purely Organic Phosphors

M. S. Kwon, D. Lee, S. Seo, J. Jung,
J. Kim* ____________ **11177 – 11181**

Tailoring Intermolecular Interactions for Efficient Room-Temperature Phosphorescence from Purely Organic Materials in Amorphous Polymer Matrices

Back Cover



A bright idea: Rationally designed strong intermolecular hydrogen and halogen bonds between a novel phosphor and a poly(vinyl alcohol) (PVA) matrix led to bright room-temperature phosphorescence (RTP) with a quantum yield of 24 %. Modulation of the strength of halogen and hydrogen bonding in the purely organic phosphor–PVA system by water enabled reversible switching between phosphorescence (green) and fluorescence (blue).

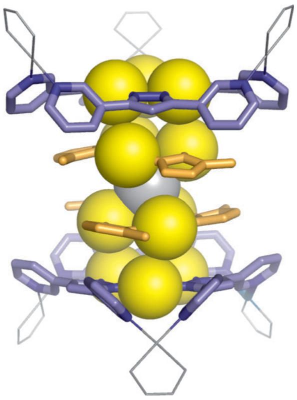
Artificial photosynthesis: A mixed-valent tetramanganese oxo core that is anchored on an inorganic polyoxotungstate ligand acts as a functional analogue of the oxygen-evolving complex of photosystem II. In the presence of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and $S_2O_8^{2-}$, the complex enables the evolution of O_2 within a light-driven catalytic cycle.

Photosynthesis

R. Al-Oweini, A. Sartorel, B. S. Bassil,
M. Natali, S. Berardi, F. Scandola,*
U. Kortz,* M. Bonchio* **11182 – 11185**

Photocatalytic Water Oxidation by a Mixed-Valent $Mn^{III}_3Mn^{IV}O_3$ Manganese Oxo Core that Mimics the Natural Oxygen-Evolving Center

Inside Cover



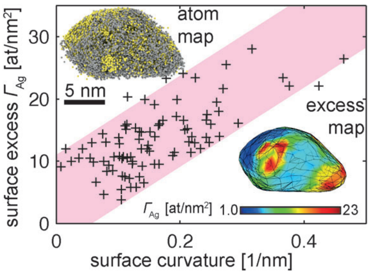
Pile up gold: A $Pd^{II}_3Au^{I}_3$ shallow concave complex was prepared by connecting peripheral pyridyl groups of a planar Au^{I}_3 complex with each other through Pd^{II} coordination. The tray-shaped host accommodated the Au^{I}_3 planes to form three-dimensional Au^{I} arrays. The number of Au^{I}_3 stacks (*n*) was systematically tuned by the solvent conditions and the addition of Ag^{I} ions.

Metal Ion Cluster

T. Osuga, T. Murase, M. Hoshino,
M. Fujita* **11186 – 11189**

A Tray-Shaped, Pd^{II}-Clipped Au_3 Complex as a Scaffold for the Modular Assembly of [3 × *n*] Au Ion Clusters

Atomic cartography: Atom-probe tomography reveals the atomic structure of Au@Ag nanoparticles. The atomic arrangement of the particle is reconstructed with a resolution of ±0.5 nm and shows that the surface coverage of Ag is influenced by the presence of residues from the synthesis. There is also a relationship between the particle's surface curvature and the Ag surface coverage (surface excess, Γ_{Ag}).

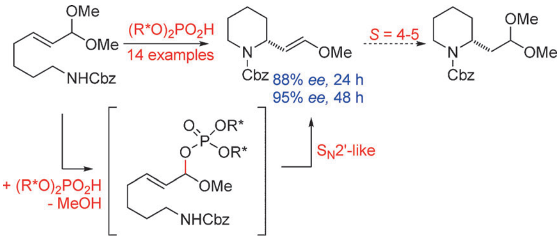


Nanoparticle Surfaces

P. Felfer, P. Benndorf, A. Masters,
T. Maschmeyer,*
J. M. Cairney **11190 – 11193**

Revealing the Distribution of the Atoms within Individual Bimetallic Catalyst Nanoparticles

Front Cover



A rich seam: An enantioselective chiral phosphoric acid-catalyzed cyclization of unsaturated acetals has been utilized for the synthesis of functionalized chiral piperidines. The chiral enol ether products of these cyclizations undergo subsequent in situ enantioenrichment. A new computational method was utilized to elucidate the mechanism and stereoselectivity of this transformation. Cbz = benzyloxycarbonyl; *S* = resolution.

Organocatalysis

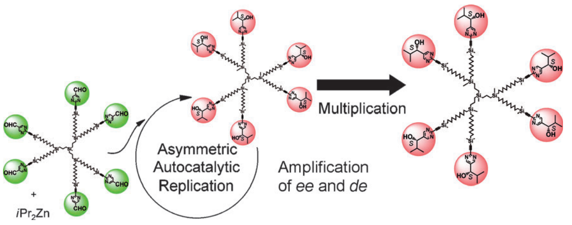
Z. Sun, G. A. Winschel,
P. M. Zimmerman,*
P. Nagorny* **11194 – 11198**

Enantioselective Synthesis of Piperidines through the Formation of Chiral Mixed Phosphoric Acid Acetals: Experimental and Theoretical Studies

Asymmetric Amplification

T. Kawasaki, M. Nakaoda, Y. Takahashi, Y. Kanto, N. Kuruhara, K. Hosoi, I. Sato, A. Matsumoto, K. Soai* **11199 – 11202**

Self-Replication and Amplification of Enantiomeric Excess of Chiral Multifunctionalized Large Molecules by Asymmetric Autocatalysis

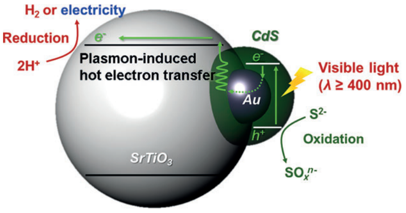


Branching out: The chiral large molecules formed from a branched hexaalkylsilane backbone asymmetrically catalyze the production of molecules with the same structure, including the chirality of newly formed asymmetric carbon atoms. The chirality of the large molecules controlled the enantioselectivity of the reaction in a highly selective manner to construct multiple asymmetric carbon centers in a single reaction.

Hot-Electron Transfer

S. Yu, Y. H. Kim, S. Y. Lee, H. D. Song, J. Yi* **11203 – 11207**

Hot-Electron-Transfer Enhancement for the Efficient Energy Conversion of Visible Light



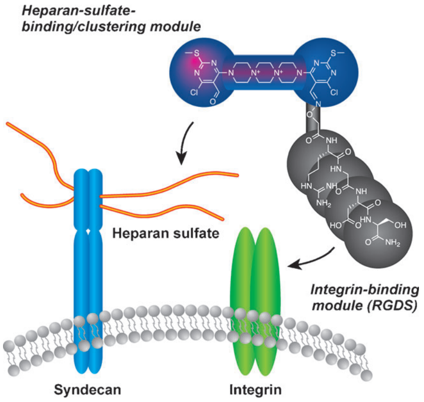
A core–shell nanostructure with three distinct components enables the efficient production of H_2 from water and significant electron harvesting under visible-light irradiation because of enhanced hot-electron injection, the formation of a Schottky junction, and high-performance electron filtering. The electron transfer pathway is elucidated through steady-state and time-resolved photoluminescence spectroscopy.

Chemical Biology

H. L. Frisco-Cabanos, M. Watanabe, N. Okumura, K. Kusamori, N. Takemoto, J. Takaya, S. Sato, S. Yamazoe, Y. Takakura, S. Kinoshita, M. Nishikawa,* N. Koizumi,* M. Uesugi* **11208 – 11213**

Synthetic Molecules that Protect Cells from Anoikis and Their Use in Cell Transplantation

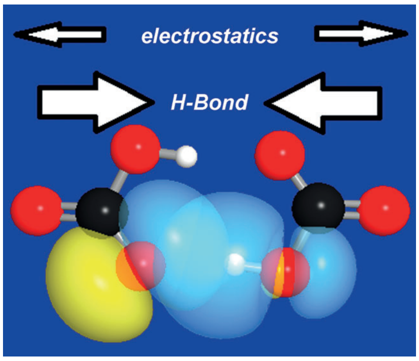
Better success in cell transplantation: New designer molecules that protect cells from detachment-induced apoptosis (anoikis) in vitro and enhance cell engraftment were tested in a type 2 diabetic mouse model and a corneal endothelial disease rabbit model. These molecules represent the first soluble synthetic dual agonist of heparan-sulfate-containing syndecan and integrin.



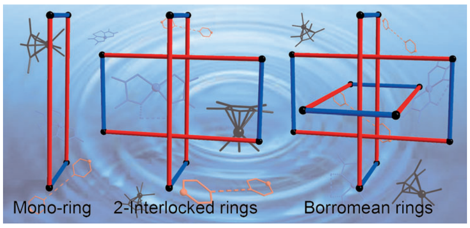
Bond Theory

F. Weinhold,* R. A. Klein **11214 – 11217**

Anti-Electrostatic Hydrogen Bonds



Challenging doctrine: New types of anion–anion or cation–cation H-bonded complexes are described that exhibit robust kinetic stability and the typical theoretical (resonance-type n_O-σ^*_{OH}), structural, and spectroscopic signatures of hydrogen bonding, despite the opposing influence of Coulomb electrostatic forces that are sometimes considered essential to H-bond formation.

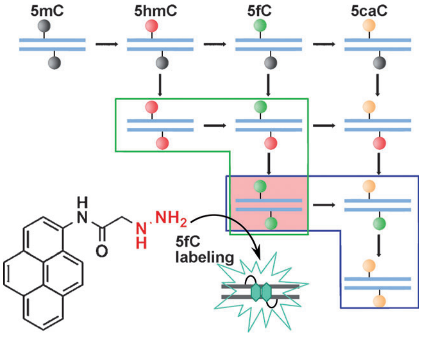


A (Borro)mean business: For chemists, molecular Borromean rings represent a formidable synthetic challenge. Different from their stepwise synthesis with the aid of a well-known driving force, a self-assembly method associated with the formation of molecular rectangles is described. DFT calculations were used to provide theoretical support for the formation of these species.

Supramolecular Chemistry

S. L. Huang, Y. J. Lin, Z. H. Li,
G. X. Jin* ———— **11218 – 11222**

Self-Assembly of Molecular Borromean Rings from Bimetallic Coordination Rectangles

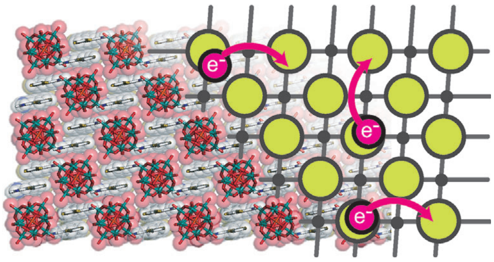


Employing the unique fluorescence properties of the pyrene group, a sensitive fluorescence-based probe was designed and synthesized not only to target 5-formylcytosine (5fC) sites, but also to distinguish symmetric from asymmetric 5fC sites in the double-stranded DNA context during the TET-dependent 5mC oxidation process. Dominant levels of symmetric 5fC were revealed among total 5fC sites during in vitro TET-dependent 5mC oxidation.

DNA Demethylation

L. Xu, Y.-C. Chen, J. Chong, A. Fin,
L. S. McCoy, J. Xu, C. Zhang,
D. Wang* ———— **11223 – 11227**

Pyrene-Based Quantitative Detection of the 5-Formylcytosine Loci Symmetry in the CpG Duplex Content during TET-Dependent Demethylation



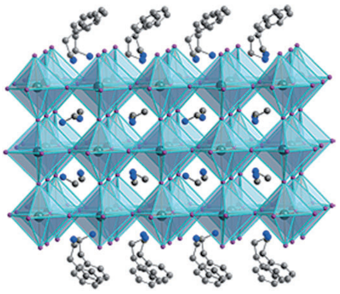
Down to the wire: In a mixed-valence polyoxometalate (POM), electrons are usually delocalized within the metal cluster anion because of a low degree of intercluster interaction. If the mixed-valence POMs are electrically linked together by wires of cationic π molecules of tetrathiafulvalene substituted with pyridinium, electron transport can occur by electron hopping as a result of the strong interactions between cluster and cationic π molecules.

Molecular Electronics

R. Tsunashima,* Y. Iwamoto, Y. Baba,
C. Kato, K. Ichihashi, S. Nishihara,
K. Inoue, K. Ishiguro, Y.-F. Song,
T. Akutagawa ———— **11228 – 11231**

Electrical Network of Single-Crystalline Metal Oxide Nanoclusters Wired by π-Molecules

Inside Back Cover



$(C_6H_5(CH_2)_2NH_3)_2(CH_3NH_3)_2[Pb_3I_{10}]$

2D Pb–I perovskites (see figure) are used as absorbers in solar cells with an open-circuit voltage of 1.18 V and a power conversion efficiency of 4.73 %. Although its 3D analogue is a promising solar-cell absorber, its instability to moisture requires anhydrous processing. 2D perovskites are more moisture resistant and devices can be fabricated in humid conditions. They may offer greater tunability at the molecular level for material optimization.

Perovskite Solar Cells

I. C. Smith, E. T. Hoke, D. Solis-Ibarra,
M. D. McGehee,
H. I. Karunadasa* ———— **11232 – 11235**

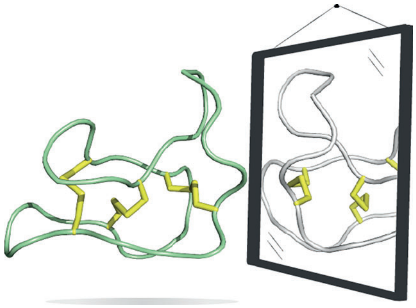
A Layered Hybrid Perovskite Solar-Cell Absorber with Enhanced Moisture Stability

Cyclic Peptides

C. K. Wang, G. J. King, S. E. Northfield,
P. G. Ojeda, D. J. Craik* **11236 – 11241**

Racemic and Quasi-Racemic X-ray Structures of Cyclic Disulfide-Rich Peptide Drug Scaffolds

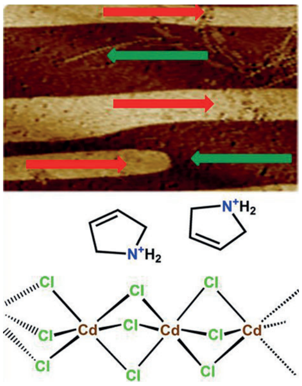
Looking into the mirror: Cyclic disulfide-rich peptides are exceptionally stable and thus promising frameworks for drug design, however, disulfide-rich peptides are notoriously difficult to crystallize. To overcome this limitation, L- and D-forms of three prototypic cyclic disulfide-rich peptides were synthesized for crystallization studies on the racemic mixtures.



Molecular Ferroelectricity

H.-Y. Ye, Y. Zhang, D.-W. Fu,
R.-G. Xiong* **11242 – 11247**

An Above-Room-Temperature Ferroelectric Organo–Metal Halide Perovskite: (3-Pyrrolinium)$(CdCl_3)$

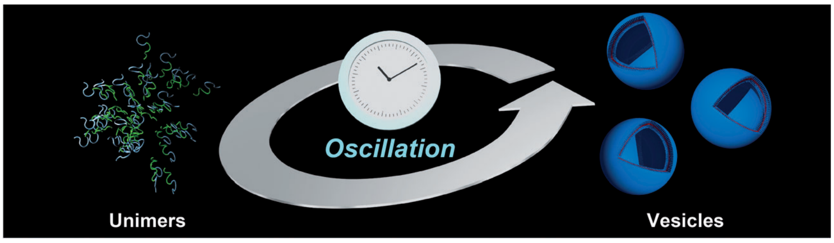


Changing phases: A hexagonal stacking organo–metal halide perovskite-type complex (3-pyrrolinium)$(CdCl_3)$ was designed. It shows above-room-temperature ferroelectricity with a Curie temperature $T_c = 316$ K, an anomalous photovoltaic effect with an open-circuit voltage of 32 V, and the formation of stripe-like electric domains as a result of spontaneous polarization measured by piezoresponse force microscopy (see picture).

Biomimetic Vesicles

R. Tamate, T. Ueki,* M. Shibayama,
R. Yoshida* **11248 – 11252**

Self-Oscillating Vesicles: Spontaneous Cyclic Structural Changes of Synthetic Diblock Copolymers

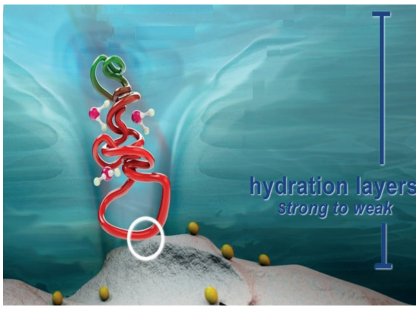


Making and breaking: Biomimetic self-oscillating vesicles that undergo autonomous and cyclic structural changes between vesicles and unimers without any external stimuli were developed by using synthetic polymers.

Wet Adhesion

Y. Akdogan, W. Wei, K.-Y. Huang,
Y. Kageyama, E. W. Danner, D. R. Miller,
N. R. Martinez Rodriguez, J. H. Waite,
S. Han* **11253 – 11256**

Intrinsic Surface-Drying Properties of Bioadhesive Proteins

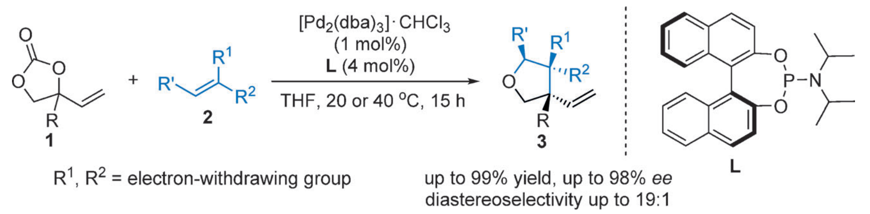


Home and dry underwater: Repulsive hydration forces hinder wet adhesion in the absence of applied external forces. The direct measurement of hydration-water dynamics by NMR relaxometry at 10 GHz revealed that the most hydrophobic mussel adhesive protein, and not the most enriched with 3,4-dihydroxyphenylalanine, effectively dries the surface and overcomes repulsive hydration forces to adsorb spontaneously to surfaces in preparation for adhesion.

Asymmetric Catalysis

A. Khan, L. Yang, J. Xu, L. Y. Jin,
Y. J. Zhang* ______ **11257 – 11260**

Palladium-Catalyzed Asymmetric Decarboxylative Cycloaddition of Vinylethylene Carbonates with Michael Acceptors: Construction of Vicinal Quaternary Stereocenters

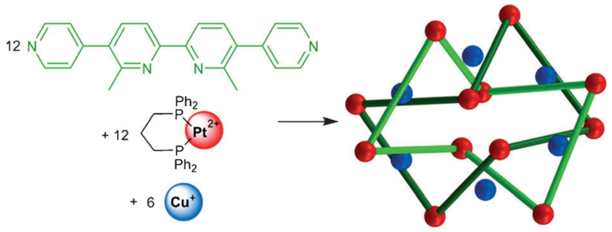


Vicinal all-carbon quaternary stereocenters are constructed through a Pd-catalyzed asymmetric decarboxylative cycloaddition of vinylethylene carbonates **1** with Michael acceptors **2** (see scheme). By using a palladium complex generated in situ from $[Pd_2(dab)_3]\cdot CHCl_3$ and phosphoramidite **L**, the process provides multifunctionalized tetrahydrofurans **3** in high yields with high levels of diastereo- and enantioselectivities.

Supramolecular Chemistry

C. Schouwey, J. J. Holstein, R. Scopelliti,
K. O. Zhurov, K. O. Nagornov,
Y. O. Tsybin, O. S. Smart, G. Bricogne,
K. Severin* ______ **11261 – 11265**

Self-Assembly of a Giant Molecular Solomon Link from 30 Subcomponents

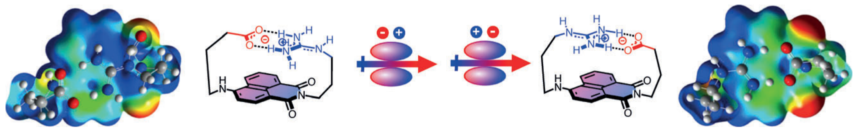


Linking with sticks: A molecular Solomon link is formed by assembly of twelve *cis*-blocked Pt^{2+} complexes, six Cu^+ ions, and twelve rigid N-donor ligands. The complex represents a molecular version of a “stick link”.

π Interactions

K. Fujisawa, C. Beuchat,
M. Humbert-Droz, A. Wilson,
T. A. Wesolowski, J. Mareda, N. Sakai,
S. Matile* ______ **11266 – 11269**

Anion–π and Cation–π Interactions on the Same Surface

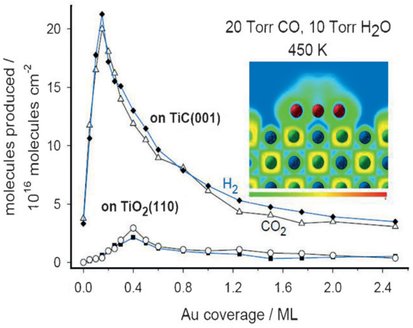


It takes two to tango: Theoretical and experimental evidence shows that anion–π and cation–π interactions can occur simultaneously on the same aromatic surface. The resulting ion pair–π interactions shift the absorption of push–pull chromophores to the red.

Hydrogen Production

J. A. Rodriguez,* P. J. Ramírez,
G.-G. Asara, F. Viñes, J. Evans, P. Liu,
J. M. Ricart, F. Illas ______ **11270 – 11274**

Charge Polarization at a Au–TiC Interface and the Generation of Highly Active and Selective Catalysts for the Low-Temperature Water–Gas Shift Reaction

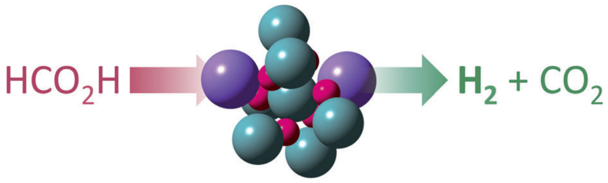


The power of association: Au atoms in contact with TiC(001) were found to undergo significant charge polarization. Strong metal–support interactions make Au/TiC(001) an excellent catalyst for the low-temperature water–gas shift (WGS), with turnover frequencies orders of magnitude larger than those observed for conventional metal/oxide catalysts (see graph). DFT calculations indicated an associative WGS mechanism, with HOCO as a key intermediate.

Formic Acid Dehydrogenation

R. I. J. Amos,* F. Heinroth, B. Chan,*
S. Zheng, B. S. Haynes, C. J. Easton,
A. F. Masters,* L. Radom,*
T. Maschmeyer* ________ **11275 – 11279**

Hydrogen from Formic Acid through Its Selective Disproportionation over Sodium Germanate—A Non-Transition-Metal Catalysis System

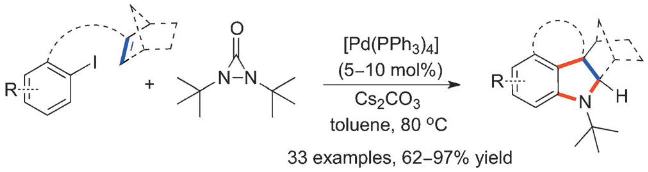


From models to reality: A robust catalyst for the selective dehydrogenation of formic acid to liberate hydrogen gas has been designed computationally, and also demonstrated experimentally. This catalyst represents an important step towards the use of renewable formic acid as a hydrogen-storage and transport vector in fuel and energy applications.

Heterocycles

H. Zheng, Y. Zhu, Y. Shi* **11280 – 11284**

Palladium(0)-Catalyzed Heck Reaction/C–H Activation/Amination Sequence with Diaziridinone: A Facile Approach to Indolines

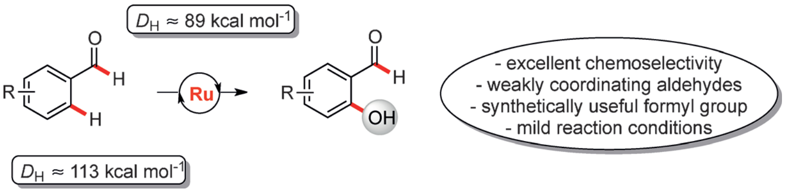


Good form: Indolines are important moieties present in various biologically significant molecules. Described is the title sequence for forming indolines with di-*tert*-butyldiaziridinone. The reaction process likely proceeds via a pallada(II)cycle, which is converted into an indoline by oxidative addition to the diaziridinone and two subsequent C–N bond formations.

C–H Activation

F. Yang, K. Rauch, K. Kettelhoit,
L. Ackermann* ________ **11285 – 11288**

Aldehyde-Assisted Ruthenium(II)-Catalyzed C–H Oxygenations



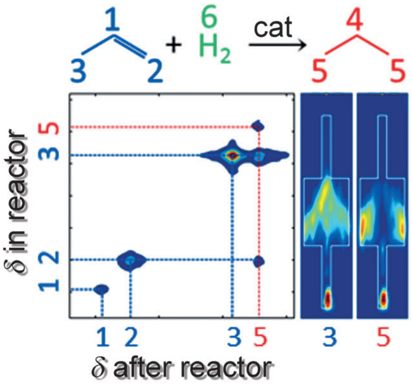
The weakest link: Challenging aryl C–H oxygenations with very weakly coordinating aldehydes proceed chemoselectively in the presence of versatile ruthenium(II) catalysts under mild reaction conditions. This transformation features an ample substrate scope and excellent positional selectivity.

Microreactor Imaging

V.-V. Telkki,* V. V. Zhivonitko, A. Selent,
G. Scotti, J. Leppäniemi, S. Franssila,
I. V. Koptyug ________ **11289 – 11293**

Lab-on-a-Chip Reactor Imaging with Unprecedented Chemical Resolution by Hadamard-Encoded Remote Detection NMR

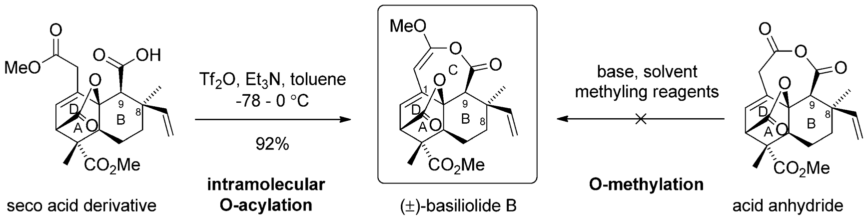
Increased NMR sensitivity: Remote detection exchange NMR spectroscopy (RD-EXSY), along with indirect spatial information extracted from time-of-flight data, provides unique information about the active regions, reaction pathways, and intermediates in a lab-on-a-chip reactor. Direct spatial resolution can be added to RD-EXSY by applying the principles of Hadamard spectroscopy.



Total Synthesis

L. Min, Y. Zhang, X. Liang, J. Huang,
W. Bao, C.-S. Lee* ______ **11294 – 11297**

A Biomimetic Synthesis of
(±)-Basiliolide B

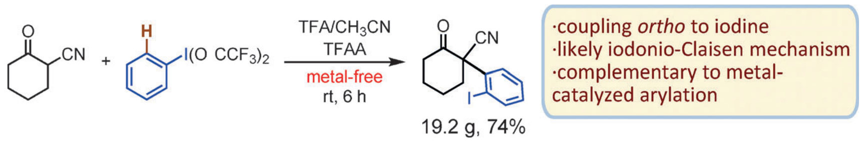


O-Acylation or O-methylation? The biosynthetic origin of the C ring of the basiliolide/transtaganolide framework has been elucidated by studying the proposed biosynthetic pathways, namely O-acylation and O-methylation. The intramolecular O-acylation of the seco acid derivative gave (±)-basiliolide B in 92 % yield. This indicates that the seco acid derivative is likely a biosynthetic precursor of basiliolide B instead of a biosynthetic dead end.

Synthetic Methods

Z. Jia, E. Gálvez, R. M. Sebastián,
R. Pleixats, Á. Álvarez-Larena, E. Martin,
A. Vallribera,* A. Shafir* _ **11298 – 11301**

An Alternative to the Classical α-Arylation:
The Transfer of an Intact 2-Iodoaryl from
$\mathrm{ArI(O_2CCF_3)_2}$



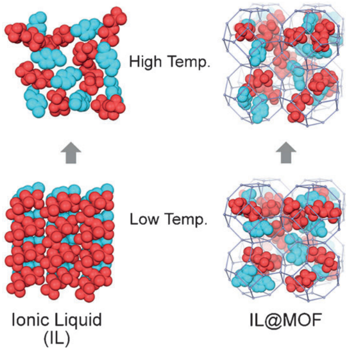
[3,3] Iodonium enolate rearrangement: Activated ketone derivatives, including β-dicarbonyl and α-cyanoketones, react with $\mathrm{ArI(O_2CCF_3)_2}$ reagents to give an α-arylated product with the iodine atom retained *ortho* to the new C—C bond. The reaction takes place under acidic conditions. This formal C—H functionalization reaction presumably proceeds through a [3,3] rearrangement of an iodonium enolate. The final α-(2-iodoaryl)ketones are versatile synthetic building blocks.

Metal–Organic Frameworks

K. Fujie,* T. Yamada, R. Ikeda,
H. Kitagawa* ______ **11302 – 11305**

Introduction of an Ionic Liquid into the
Micropores of a Metal–Organic
Framework and Its Anomalous Phase
Behavior

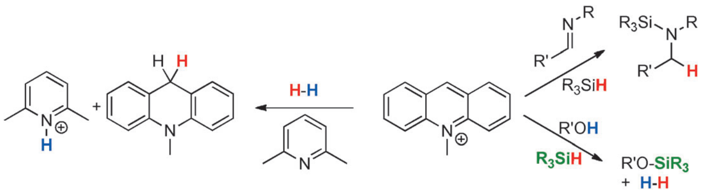
Hosting ionic guests: An ionic liquid (IL) was incorporated within the micropores of a metal–organic framework (MOF). The phase behavior of the IL inside the MOF micropores was studied by differential scanning calorimetry and solid-state NMR measurements. The IL inside the micropores demonstrated no marked freezing transition down to low temperature, where the bulk IL was frozen.



Synthetic Methods

E. R. Clark,
M. J. Ingleson* ______ **11306 – 11309**

N-Methylacridinium Salts: Carbon Lewis
Acids in Frustrated Lewis Pairs for σ-Bond
Activation and Catalytic Reductions

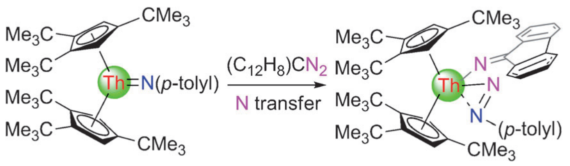


Softly does it: *N*-methylacridinium salts are shown to be versatile Lewis acids within frustrated Lewis pairs for stoichiometric and catalytic transformations by through H_2 activation.

Actinide Chemistry

W. Ren, E. Zhou, B. Fang, G. Hou, G. Zi,*
D.-C. Fang,*
M. D. Walter* ________ **11310 – 11314**

Experimental and Computational Studies on the Reactivity of a Terminal Thorium Imidometallocene towards Organic Azides and Diazoalkanes

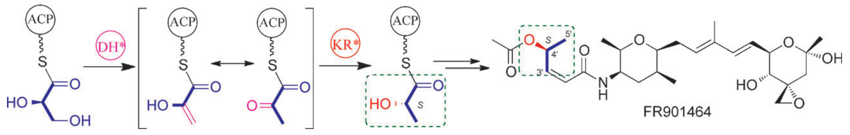


A hard act(inide) to follow: The reaction of a thorium imido complex with 9-diazofluorene was found to proceed through a [2+2] cycloaddition reaction to yield a η^2-diazenido iminato complex (see scheme). In contrast, an organic azide reacted with the same thorium imido complex by [2+3] cycloaddition to give a tetraazametallacyclopentene.

Polyketide Biosynthesis

H.-Y. He, H. Yuan, M.-C. Tang,
G.-L. Tang* ________ **11315 – 11319**

An Unusual Dehydratase Acting on Glycerate and a Ketoreducatse Stereoselectively Reducing α-Ketone in Polyketide Starter Unit Biosynthesis

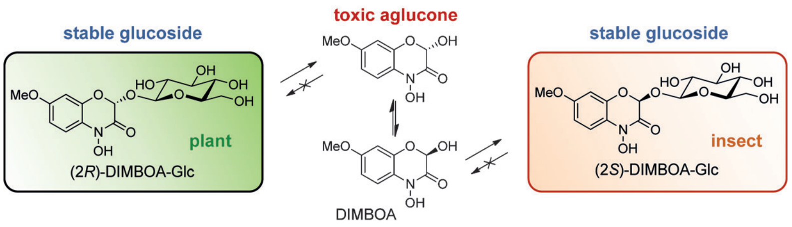


Biochemical characterization of a dehydratase and a ketoreductase-like domain (DH*-KR*) in the loading module of FR901464 polyketide synthase revealed that DH* catalyzes the dehydration of an acyl carrier protein (ACP)-tethered glycerate to an ACP-linked pyruvate. The KR* domain then carries out α-ketone reduction to yield L-lactyl-*S*-ACP, which serves as a starter unit for polyketide biosynthesis.

Chemical Ecology

F. C. Wouters, M. Reichelt, G. Glauser,
E. Bauer, M. Erb, J. Gershenzon,
D. G. Vassão* ________ **11320 – 11324**

Reglucosylation of the Benzoxazinoid DIMBOA with Inversion of Stereochemical Configuration is a Detoxification Strategy in Lepidopteran Herbivores



Through the looking-glass: Grasses produce benzoxazinoid (BXD) glucosides as a chemical defense against herbivores. (2*R*)-DIMBOA-Glc, the major BXD in maize, is hydrolyzed by glucosidases upon herbivory to yield the toxic aglucone DIMBOA. However the caterpillars of some *Spodoptera* species elegantly deactivate this toxin through stereospecific reglucosylation to give (2*S*)-DIMBOA-Glc, an epimer of the plant compound that is inert towards maize glucosidases.

[4+2] Cycloaddition

K. Komeyama,* Y. Okamoto,
K. Takaki ________ **11325 – 11328**

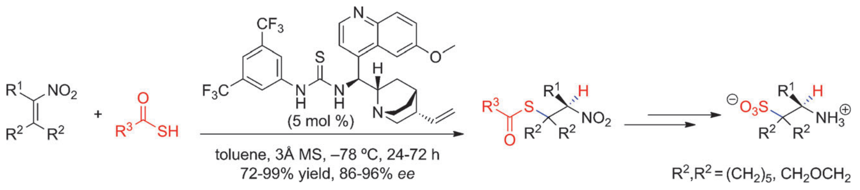
Cobalt-Catalyzed Formal [4+2] Cycloaddition of α,α′-Dichloro-*ortho*-Xylenes with Alkynes

Simple, but powerful: The title reaction leads to 1,4-dihydronaphthalenes with a wide substrate scope and high functional-group tolerance. Mechanistic investigation supports a benzyl cobaltation of alkyne, not the classical Diels–Alder reaction of *ortho*-quinodimethanes. This methodology provides a straightforward access to linearly expanded π-conjugated aromatics.

Organocatalysis

J. P. Phelan, E. J. Patel,
J. A. Ellman* ——— 11329 – 11332

Catalytic Enantioselective Addition of Thioacids to Trisubstituted Nitroalkenes

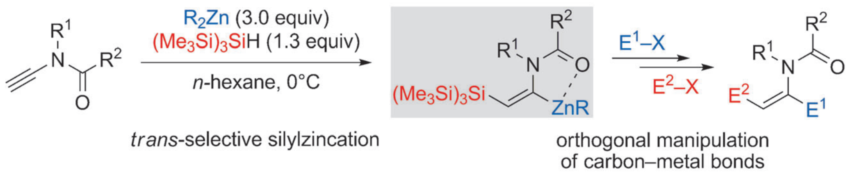


High enantioselectivities and excellent yields are obtained in the first example of a catalytic enantioselective addition to and nitronate protonation of trisubstituted nitroalkenes, generating a tetrasubstituted carbon atom. Thioacids reacted with both activated and unactivated nitroalkenes. The 1,2-nitrothioacetate products can be readily converted in two steps to biomedically relevant 1,2-aminosulfonic acids without loss of enantiopurity.

Radical Chemistry

E. Romain, C. Fopp, F. Chemla, F. Ferreira,
O. Jackowski, M. Oestreich,*
A. Perez-Luna* ——— 11333 – 11337

Trans-Selective Radical Silylzincation of Ynamides

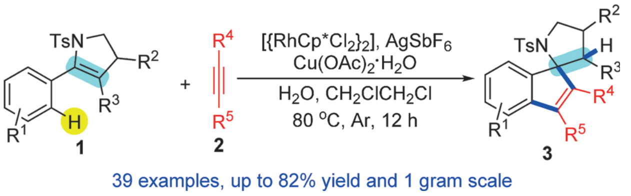


A radical *trans*formation: *Z*-configured α,β-disubstituted enamides are obtained through a regio- and stereoselective silylzincation of terminal ynamides and subsequent sequential functionalization of the resulting C_{sp^2}–Zn and C_{sp^2}–Si bonds (see scheme). The *trans*-selective silylzincation proceeds through a radical process combining organosilyl radical and radical Zn-atom transfer chemistry.

Heterocycle Synthesis

M.-B. Zhou, R. Pi, M. Hu, Y. Yang,
R.-J. Song, Y. Xia,*
J.-H. Li* ——— 11338 – 11341

Rhodium(III)-Catalyzed [3+2] Annulation of 5-Aryl-2,3-dihydro-1*H*-pyrroles with Internal Alkynes through C(sp²)–H/Alkene Functionalization



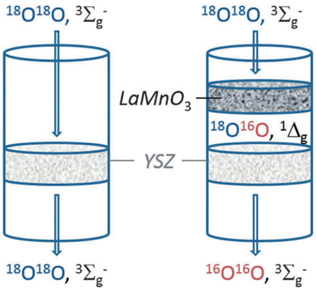
Spiral bound: A new [3+2] annulation route to spiro[indene-1,2′-pyrrolidines] includes C(sp²)–H functionalization, insertion of an alkyne, addition of a C=C bond, and protonolysis to assemble a spirocyclic ring system. The method has a broad range of functional-group tolerance and excellent regioselectivity. Ts = 4-toluenesulfonyl.

Heterogeneous Catalysis

M. Richard, F. Can, D. Duprez, S. Gil,
A. Giroir-Fendler,
N. Bion* ——— 11342 – 11345

Remarkable Enhancement of O_2 Activation on Yttrium-Stabilized Zirconia Surface in a Dual Catalyst Bed

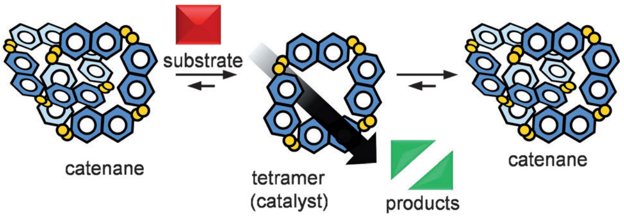
A double bed is better: The exchange of O_2 across an $LaMnO_3$ catalytic bed leads to an enhancement of its activation on an yttrium-stabilized zirconia (YSZ) surface. The O atoms of the YSZ lattice, which are unable to exchange with gas-phase O_2 below 823 K, become exchangeable from 533 K in a dual $LaMnO_3$-YSZ bed. This property makes the dual $LaMnO_3$-Pd/YSZ catalytic system highly active for CH_4 combustion and partial oxidation at moderate temperatures.



Systems Catalysis

H. Fanlo-Virgós, A.-N. R. Alba, S. Hamieh,
M. Colomb-Delsuc,
S. Otto* ______________ 11346 – 11350

Transient Substrate-Induced Catalyst Formation in a Dynamic Molecular Network

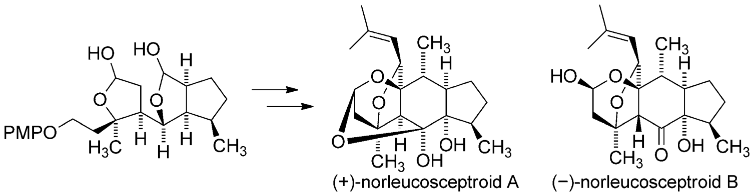


Substrate-induced catalyst formation was achieved which is similar to the continuous regulation of enzymes in biology. A dynamic molecular network responds to the substrate by transiently producing the catalyst required for its transformation. As soon as the substrate is consumed, the network disassembles the catalyst again. These results open up new opportunities for controlling catalysis in synthetic chemical systems.

Terpenoid Synthesis

C. L. Hugelshofer,
T. Magauer* ______________ 11351 – 11355

A General Entry to Antifeedant Sesterterpenoids: Total Synthesis of (+)-Norleucosceptroid A, (−)-Norleucosceptroid B, and (−)-Leucosceptroid K

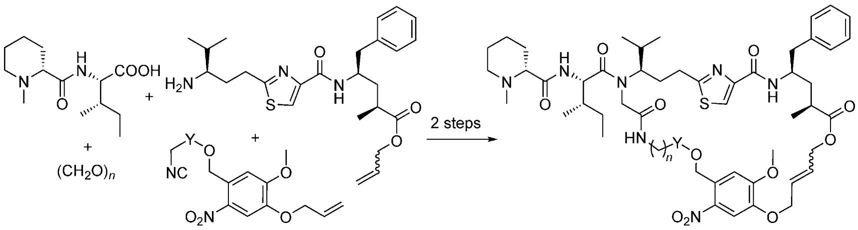


Totally terpenoid: A general asymmetric synthetic route to antifeedant leucosceptroids was developed. Highlights are a stereoselective annulation reaction and an unprecedented intramolecular dilactol condensation to construct the tricyclic carbon skeleton. The convergent approach enabled us to synthesize multigram quantities of an advanced intermediate, which was converted into (+)-norleucosceptroid A, (−)-norleucosceptroid B, and (−)-leucosceptroid K.

Photoactivation

J. Hoffmann,
U. Kazmaier* ______________ 11356 – 11360

A Straightforward Approach towards Cyclic Photoactivatable Tubulysin Derivatives

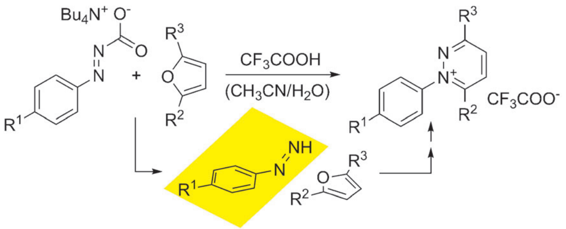


Photocleavable isocyanides can easily be obtained in a few steps from vanillin. These intermediates can be converted by an Ugi reaction and subsequent ring-closing metathesis into cyclic photocleavable natural product derivatives, as illustrated for some tubulysin derivatives.

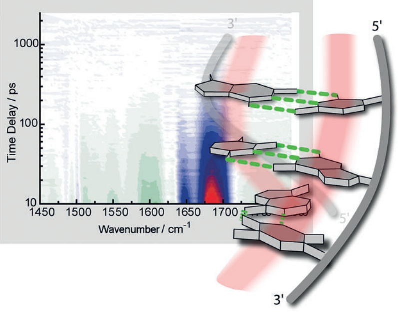
Cycloadditions

S. K. Fehler, G. Pratsch,
M. R. Heinrich* ________ 11361 – 11365

The Trapping of Phenyldiazenes in Cycloaddition Reactions



Catch me if you can! Phenyldiazenes were intensively investigated in the late 1960s. But only recently was it possible to finally trap these reactive intermediates in cycloaddition reactions leading to pyridazinium salts (see scheme).

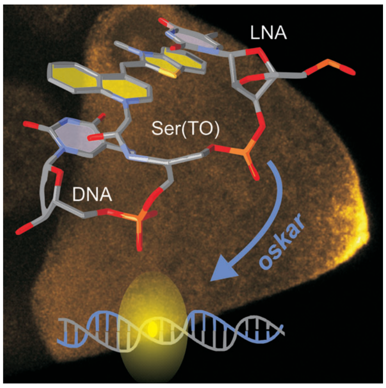


Shedding light on DNA: The excited-state dynamics of each nucleobase in calf thymus DNA following UV excitation could be determined with femtosecond IR spectroscopy. It was shown that the Watson–Crick base pairing opens up a new excited-state decay channel in double-stranded DNA, an effect that deactivates charge-transfer states.

DNA Photochemistry

D. B. Bucher, A. Schlueter, T. Carell,* W. Zinth* ______ **11366 – 11369**

Watson–Crick Base Pairing Controls Excited-State Decay in Natural DNA



...And there was light: Local constraint of the DNA structure through the introduction of a locked nucleic acid (LNA) closes fluorescence decay channels of an environment-sensitive thiazole orange dye in DNA hybridization probes. Two singly labeled LNA-enhanced forced-intercalation (FIT) probes were sufficient for tracking ribonucleotide particles in living tissue.

RNA Imaging

F. Hövelmann, I. Gaspar, S. Loibl, E. A. Ermilov, B. Röder, J. Wengel, A. Ephrussi, O. Seitz* ______ **11370 – 11375**

Brightness through Local Constraint—LNA-Enhanced FIT Hybridization Probes for In Vivo Ribonucleotide Particle Tracking

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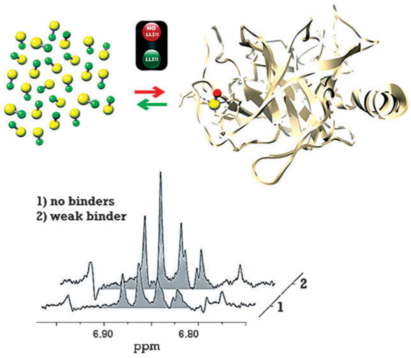
Ligands with an affinity for selected proteins can be screened very effectively by exploiting long-lived states (LLS) in NMR spectroscopy. This approach allows ligands with a wide range of affinities (10 nM < K_D < 12 mM) to be characterized. The LLS method was used to measure the dissociation constants of fragments that bind weakly to the ATP binding domain of heat shock protein Hsp90, a therapeutic target for cancer treatment.



Fragment-Based Drug Discovery

R. Buratto,* D. Mammoli, E. Chiarparin, G. Williams, G. Bodenhausen ______ **11376 – 11380**

Exploring Weak Ligand–Protein Interactions by Long-Lived NMR States: Improved Contrast in Fragment-Based Drug Screening

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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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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

Ultrafast Energy Transfer to Liquid Water by Sub-Picosecond High-Intensity Terahertz Pulses: An Ab Initio Molecular Dynamics Study

P. K. Mishra, O. Vendrell,*
R. Santra ______________ **13685–13687**

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

DOI: 10.1002/anie.201305991

The application of an external electric field in the calculations described in this Communication has been based on the usual position gauge formalism which is only adequate for non-periodic systems. In the present case, this leads to an artificially high amount of energy transfer from the electric field to the liquid at a given field intensity.

This issue was overcome by using the correct Berry phase formalism for electric fields in periodic boundary conditions as implemented in the CP2K program. The temperature jump is now achieved at an intensity of 5×10^{12} W cm^{-2} instead of 10^{10} W cm^{-2} as reported in the Communication. No ionization is found at this intensity during the pulse and therefore the conclusions remain unaffected.

The Supporting Information provided along with this Corrigendum contains new Figures 1 and 3 with corrected mean energies and corresponding distributions of the water monomers and radial distribution functions.

The authors sincerely apologize for this mistake which does not affect the main conclusions of the work.