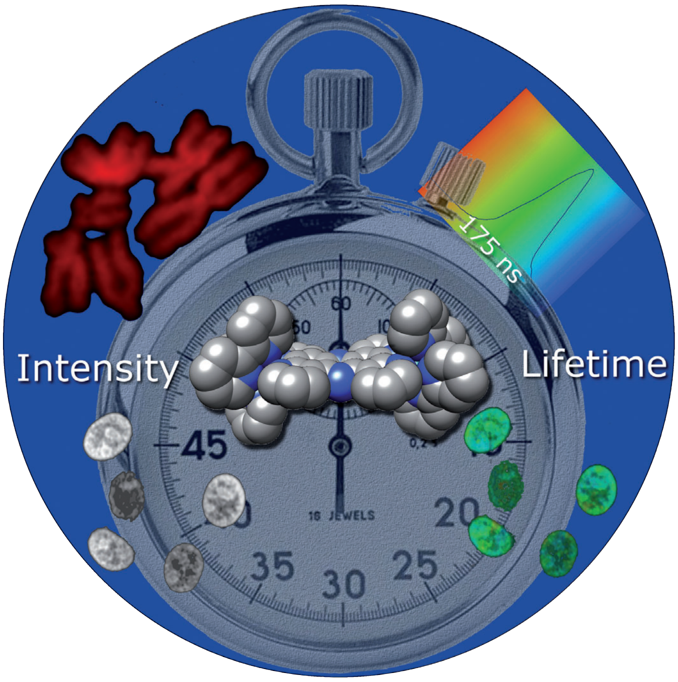
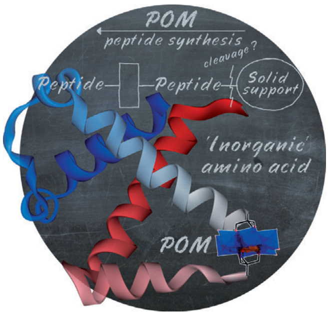
Using two-photon absorption ...

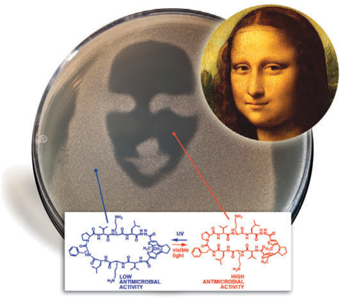


... ruthenium complexes that bind to nuclear DNA in fixed or living cells can be photoexcited within the biological optical window. In their Communication on page 3367 ff., J. A. Thomas and co-workers show that the long-lived ^{3}MLCT emission of these "light-switch" complexes (> 100 ns) means that they are also phosphorescence lifetime imaging microscopy (PLIM) probes.

POM–Peptide Hybrids

In their Communication on page 3336 ff., L. Cronin et al. describe the incorporation of polyoxometalates (POMs) into peptides, which was achieved by the use of activated precursors and either a solution- or a solid-phase method.



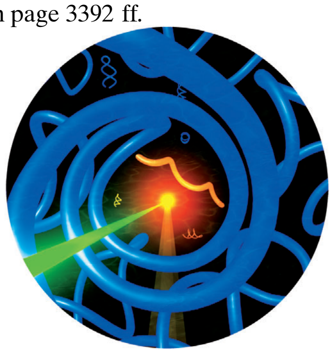


Photoswitches

A S. Ulrich, I V. Komarov, and co-workers report a photoswitchable analogue of the cyclic antimicrobial peptide gramicidin S based on a reversibly photoisomerizable diarylethene scaffold in their Communication on page 3392 ff.

Single-Molecule Thermometry

In their Communication on page 3470 ff., H. Mao et al. describe how the temperature variation in a yoctoliter volume can be measured by exploiting the mechanochemical properties of individual DNA hairpins.



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Service

Author Profile

“My motto is ‘There’s no such thing as a free lunch’. My favorite drink is green tea. …”
This and more about Markus Zweckstetter can be found on page 3306.

News

R. Nolte

L. F. Tietze

A. B. Holmes

W. B. Tolman

M. Mauduit

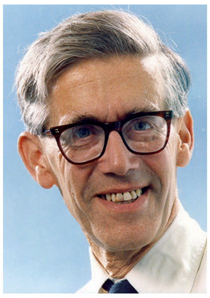
F. Caijo

S. Huber

A. Bousseksou

O. Eisenstein

Obituaries



Peter L. Pauson passed away at the age of 88 on December 10, 2013. He was well-known worldwide as one of the discoverers of ferrocene and the Pauson–Khand reaction.

Peter Ludwig Pauson (1925–2013)

*H. Werner** ____________ ***3309***

Books

Polymer Electronics

Mark Geoghegan, Georges Hadziioannou

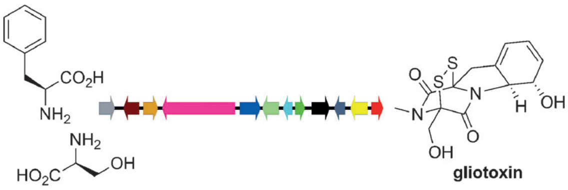
reviewed by P. J. Skabara,
N. J. Findlay ____________ **3310**

Highlights

Gliotoxin Biosynthesis

T. Amatov, U. Jahn* ______ **3312 – 3314**

Gliotoxin: Nature's Way of Making the Epidithio Bridge

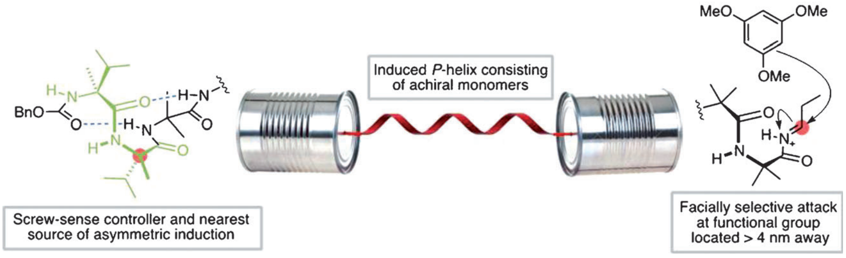


GliTzy biosynthesis! A detailed picture of the key transformations during the biogenesis of gliotoxin has recently been created. Almost every intermediate in the biosynthetic pathway and the pertinent enzymatic machinery was isolated and fully characterized, thus placing the unique incorporation of the sulfur atoms as well as the formation of the epidithio bridge catalyzed by the key enzyme GliT and its consequences into the limelight.

Remote Stereocontrol

C. P. Johnston,
M. D. Smith* ____________ **3315 – 3317**

Remote Stereocontrol Transmitted through Helicity



Induced *P*-helix consisting of achiral monomers

Screw-sense controller and nearest source of asymmetric induction

Facially selective attack at functional group located > 4 nm away

Near…far…wherever you are! Two chiral residues at the N-terminus of a helical foldamer are sufficient to induce a significant helical screw-sense preference. The capacity of this helix to transmit stereochemical information is exemplified by highly stereoselective transformations conducted over nanometer distances.

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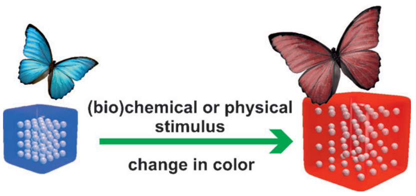
Reviews

Sensor Materials

C. Fenzl, T. Hirsch,
O. S. Wolfbeis* ______ 3318–3335

Photonic Crystals for Chemical Sensing and Biosensing



Sense and sensitivity: Nature knew them for millions of years before they were rediscovered by mankind: photonic crystals. Some butterflies and beetles use them for mimicry and survival techniques, for example to distract predators. This Review describes the mode of action of photonic crystals as well as their application for the optical chemo- and biosensing of analytes, with a focus on the materials used.

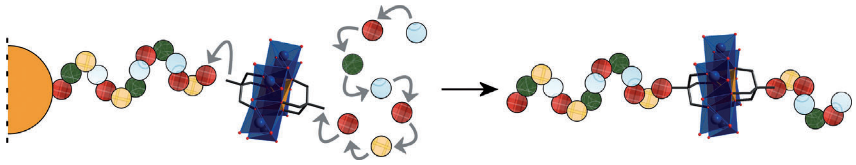
Communications

POM–Peptide Hybrids

C. Yvon, A. J. Surman, M. Hutin, J. Alex,
B. O. Smith, D.-L. Long,
L. Cronin* ______ 3336–3341

Polyoxometalate Clusters Integrated into Peptide Chains and as Inorganic Amino Acids: Solution- and Solid-Phase Approaches

Frontispiece

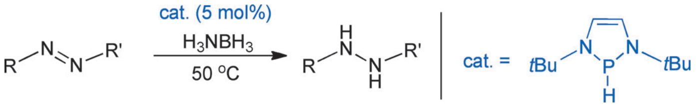


Pepping up POMs: The incorporation of polyoxometalates (POMs) into peptides was realized by the use of activated precursors. Using a solution-phase approach, pre-synthesized peptides can be grafted onto the metal oxide cluster to produce hybrids of unprecedented scale. An adapted solid-phase method allows direct incorporation of these clusters during peptide synthesis as hybrid unnatural amino acids.

Hydrogen Transfer

C.-C. Chong, H. Hirao,*
R. Kinjo* ______ 3342–3346

A Concerted Transfer Hydrogenolysis: 1,3,2-Diazaphospholene-Catalyzed Hydrogenation of N=N Bond with Ammonia–Borane



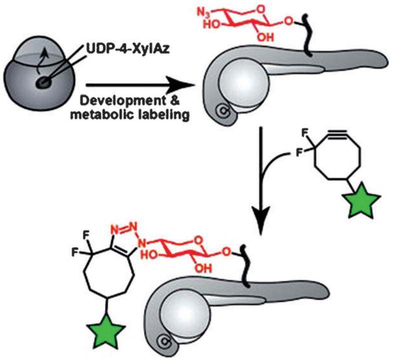
On the double: Diazaphospholenes catalyze the transfer hydrogenation of a N=N bond under mild reaction conditions, allowing access to various hydrazine derivatives. The catalytic cycle involves two key steps, and the catalyst maintains the P^{III} oxidation state throughout the catalytic cycle. The reaction mechanism involves a hydrogenolysis of the exocyclic P–N bond of the intermediate by ammonia–borane, and it proceeds in a concerted double-hydrogen-transfer fashion.

Glycosylation Inhibitor

B. J. Beahm, K. W. Dehnert, N. L. Derr,
J. Kuhn, J. K. Eberhart, D. Spillmann,
S. L. Amacher,
C. R. Bertozzi* ______ 3347–3352

A Visualizable Chain-Terminating Inhibitor of Glycosaminoglycan Biosynthesis in Developing Zebrafish

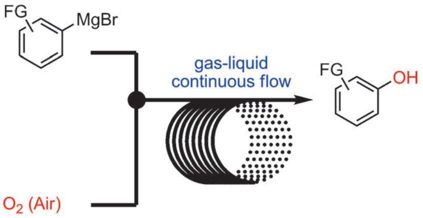
Visualizing inhibition: Metabolic incorporation of an azide modified xylose residue inhibits elaboration of the glycan. Further, the azide group enables rapid visualization of the sites of inhibition in vivo during zebrafish development using Cu-free click chemistry.



Synthetic Methods

Z. He, T. F. Jamison* ______ **3353 – 3357**

Continuous-Flow Synthesis of Functionalized Phenols by Aerobic Oxidation of Grignard Reagents

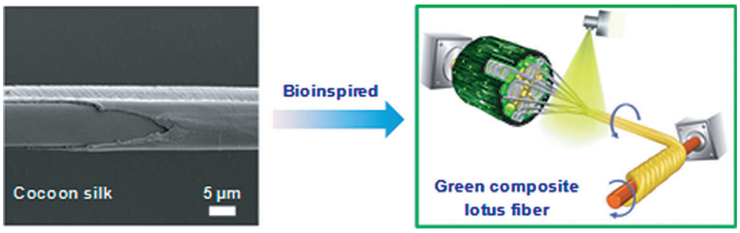


Putting on airs: Aerobic oxidation of (hetero)aryl Grignard reagents using compressed air proceeds with a gas-liquid continuous-flow system, thus enabling preparation of fucntionalized phenols. By integrating an in-line generation of ArMgBr intermediates with the aerobic oxidation, *ortho*-functionalized phenols can be assembled. The method demonstrates good functional-group (FG) compatibility, mild reaction conditions, and short reaction times.

Composite Fibers

M. X. Wu, H. Shuai, Q. F. Cheng,*
L. Jiang ______ **3358 – 3361**

Bioinspired Green Composite Lotus Fibers

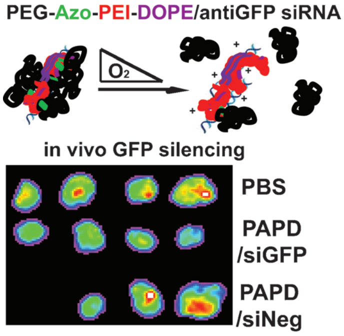


Inspired by the composite structure of cocoon silk, a green composite fiber was continuously fabricated by combining lotus fiber and poly(vinyl alcohol). Its specific mechanical properties are superior to those of cocoon silk and other natural fibers, such as jute, cotton, sisal, and ramie.

Tumor Targeting

F. Perche, S. Biswas, T. Wang, L. Zhu,
V. P. Torchilin* ______ **3362 – 3366**

Hypoxia-Targeted siRNA Delivery

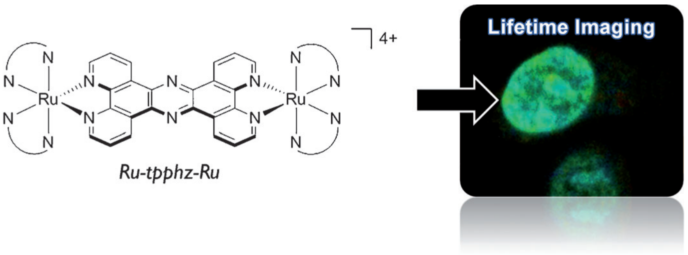


Self-assembled nanoformulations like PEG-Azobenzene-PEI-DOPE/siRNA (PAPD/siRNA) achieved hypoxia-specific GFP downregulation in vitro and GFP downregulation in GFP-expressing tumors in vivo after intravenous administration and charge exposure (see picture). By contrast, no hypoxia specificity was observed with the nonresponsive PEG-PEI-DOPE/siRNA complexes.

DNA Imaging

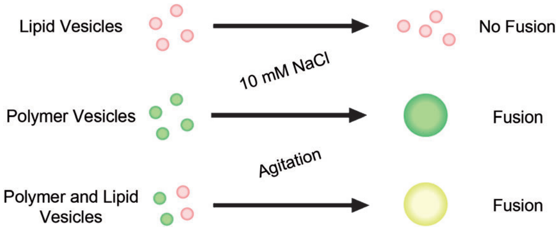
E. Baggaley, M. R. Gill, N. H. Green,
D. Turton, I. V. Sazanovich,
S. W. Botchway, C. Smythe, J. W. Haycock,
J. A. Weinstein,*
J. A. Thomas* ______ **3367 – 3371**

Dinuclear Ruthenium(II) Complexes as Two-Photon, Time-Resolved Emission Microscopy Probes for Cellular DNA



A stopwatch for DNA: Dinuclear ruthenium(II) luminophores function as two-photon phosphorescent lifetime imaging microscopy probes. These specifically image DNA and even individual chromosomes in cells.

Front Cover

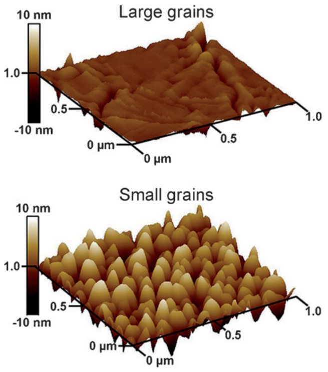


Lightly seasoned: Vesicles composed of poly(ethylene oxide)-*b*-poly(butadiene) fuse in dilute NaCl solution with mild agitation. While DOPC liposomes do not fuse under the same conditions, this unexpectedly simple approach facilitates the creation of giant hybrid polymer/lipid vesicles, paving the way for mechanically responsive nanoreactors and drug-delivery vehicles.

Polymersomes

I. M. Henderson,
W. F. Paxton* ____________ **3372 – 3376**

Salt, Shake, Fuse—Giant Hybrid Polymer/ Lipid Vesicles through Mechanically Activated Fusion



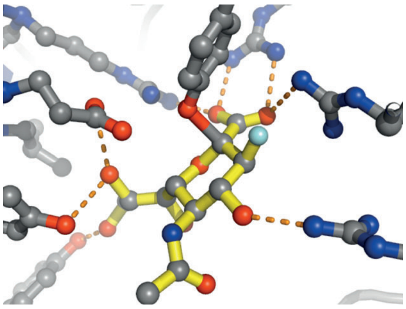
Taking the rough with the smooth: The tunneling decay coefficient β in tunneling junctions with self-assembled *n*-alkanethiolate monolayers can be controlled by changing the topography of the bottom electrodes. Rough surfaces with large areas of exposed grain boundaries give $\beta = 0.4$–$0.5\ n_C^{-1}$, while smooth surfaces with small areas of exposed grain boundaries give $\beta = 1.0\ n_C^{-1}$ (see picture).

Molecular Electronics

L. Yuan, L. Jiang, B. Zhang,
C. A. Nijhuis* ____________ **3377 – 3381**

Dependency of the Tunneling Decay Coefficient in Molecular Tunneling Junctions on the Topography of the Bottom Electrodes

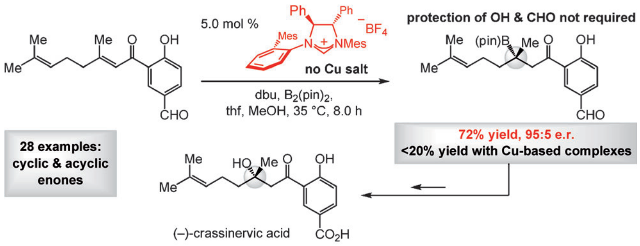
Understanding reactivity and selectivity: The mechanistic basis for the surprisingly different rates of inactivation and reactivation of human and *Trypanosoma cruzi* sialidases by the two 3-fluoro epimers of 2,3-difluorosialic acid was probed through spontaneous hydrolysis kinetics, computational analysis, and X-ray crystallography.



Biochemistry

S. Buchini, F.-X. Gallat, I. R. Greig,
J.-H. Kim, S. Wakatsuki, L. M. G. Chavas,*
S. G. Withers* ____________ **3382 – 3386**

Tuning Mechanism-Based Inactivators of Neuraminidases: Mechanistic and Structural Insights



No copper, no problem: Lewis base catalyzed enantioselective conjugate additions of (pinacolato)boron units to cyclic or acyclic enones afford products having boron-substituted quaternary carbon stereogenic centers. The reactions are promoted by a readily accessible chiral carbene and their reactivity/selectivity profiles are complementary to those of the Cu-catalyzed variants. The reaction serves as a key step in the synthesis of (−)-crassinervic acid.

Enantioselective Catalysis

S. Radomkit,
A. H. Hoveyda* ____________ **3387 – 3391**

Enantioselective Synthesis of Boron-Substituted Quaternary Carbon Stereogenic Centers through NHC-Catalyzed Conjugate Additions of (Pinacolato)boron Units to Enones

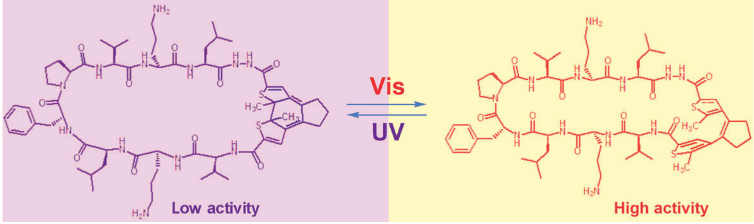
VIP

Photoswitches

O. Babii, S. Afonin, M. Berditsch,
S. Reißer, P. K. Mykhailiuk,
V. S. Kubyshkin, T. Steinbrecher,
A. S. Ulrich,* I. V. Komarov* **3392 – 3395**

Controlling Biological Activity with Light: Diarylethene-Containing Cyclic Peptidomimetics

Inside Back Cover

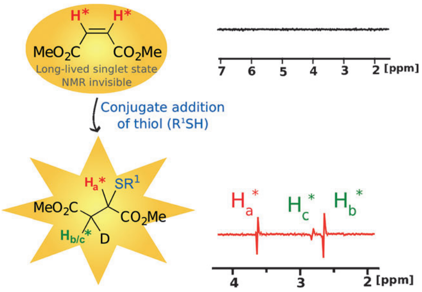


Making light work: An amino acid analogue based on a reversibly photoisomerizable diarylethene scaffold was incorporated into the cyclic backbone of the antimicrobial peptide gramicidin S. The biological activity of the resulting peptidomimetics could be effectively controlled by ultraviolet/visible light within strictly defined spatial and temporal limits.

Long-Lived Spin States

Y. Zhang, P. C. Soon, A. Jerschow,*
J. W. Canary* ———————— **3396 – 3399**

Long-Lived ^{1}H Nuclear Spin Singlet in Dimethyl Maleate Revealed by Addition of Thiols

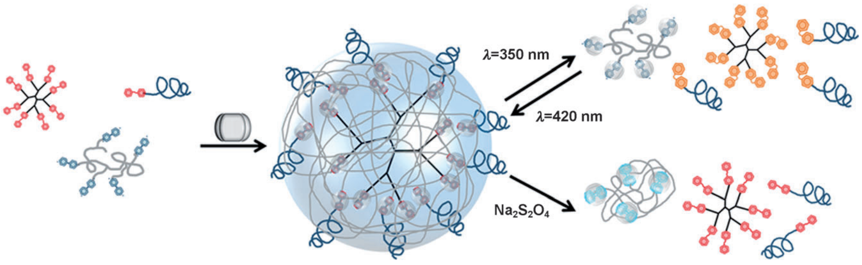


Hyperpolarized singlet states are well isolated from the environment, such that they acquire long lifetimes. Here, we used the thiol conjugate addition to unveil the hyperpolarized long-lived singlet state in deuterated dimethyl maleate (see picture). Singlet lifetimes of 4.7 min for ^{1}H spins in [D$_4$]MeOH are seen in this system.

Self-Assembled Systems

C. Stoffelen, J. Voskuhl, P. Jonkheijm,
J. Huskens* ———————— **3400 – 3404**

Dual Stimuli-Responsive Self-Assembled Supramolecular Nanoparticles

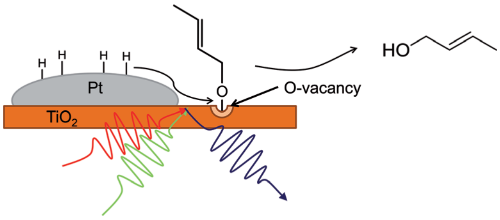


A guiding light: UV/Vis irradiation and chemical reduction have been used for the reversible disassembly/reassembly and irreversible disintegration, respectively, of responsive supramolecular nanoparticles stabilized by ternary host–guest complexes (see picture). The disassembly proceeds through an initial aggregation phase that is attributed to different response times of the multivalent core and the monovalent shell upon photoswitching.

Heterogeneous Catalysis

G. Kennedy, L. R. Baker,
G. A. Somorjai* ———————— **3405 – 3408**

Selective Amplification of C=O Bond Hydrogenation on Pt/TiO$_2$: Catalytic Reaction and Sum-Frequency Generation Vibrational Spectroscopy Studies of Crotonaldehyde Hydrogenation



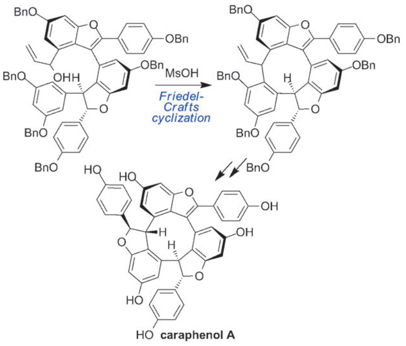
Surface activity: Sum-frequency generation vibrational spectroscopy was employed to determine the role of oxide supports in platinum-catalyzed crotonaldehyde hydrogenation. A unique species was observed on the Pt/TiO$_2$ catalysts, thus explaining the dramatic difference in catalytic activity and selectivity when compared to those of Pt/SiO$_2$.

Natural Product Synthesis

N. E. Wright, S. A. Snyder* **3409 – 3413**

9-Membered Carbocycle Formation: Development of Distinct Friedel–Crafts Cyclizations and Application to a Scalable Total Synthesis of (±)-Caraphenol A

Fun with Friedel–Crafts: Explorations into 9-membered carbocycle formation have afforded the first 9-*exo*-dig ring closure via a Au^{III}-promoted reaction between an alkyne and an aryl ring along with several additional, unique Friedel–Crafts-type cyclizations. Application of one of the 9-membered ring closures enabled an efficient and scalable (600 mg) synthesis of the resveratrol trimer caraphenol A in an average yield of 89% per step.

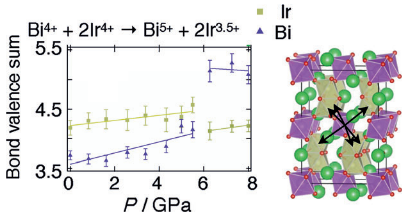


Metal Oxides

Z. Huang, J. E. Auckett, P. E. R. Blanchard, B. J. Kennedy, W. Miiller, Q. Zhou, M. Avdeev, M. R. Johnson, M. Zbiri, G. Garbarino, W. G. Marshall, Q. Gu, C. D. Ling* **3414 – 3417**

Pressure-Induced Intersite Bi–M (M = Ru, Ir) Valence Transitions in Hexagonal Perovskites

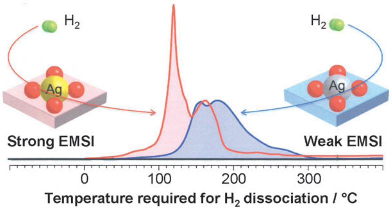
Pressure-induced charge transfer from one element to another in three hexagonal perovskites represent the first such transitions involving 4d or 5d metals, and double the total number ever observed. Electrons can be "squeezed" from the 6s shell of Bi into the 4d or 5d shells of Ru/Ir, resulting in a 1% volume reduction that becomes favorable above 5 GPa.



Metal–Support Interactions

P. Hu, Z. Huang, Z. Amghouz, M. Makkee, F. Xu, F. Kapteijn, A. Dikhtiarenko, Y. Chen, X. Gu, X. Tang* **3418 – 3421**

Electronic Metal–Support Interactions in Single-Atom Catalysts



Electronic metal–support interactions (EMSI): A supported single-atom silver catalyst with a controllable electronic state has been developed. An electronic perturbation of the catalytic sites that is induced by subtle changes in the structure of the support has a crucial influence on the intrinsic reactivity of the catalyst.

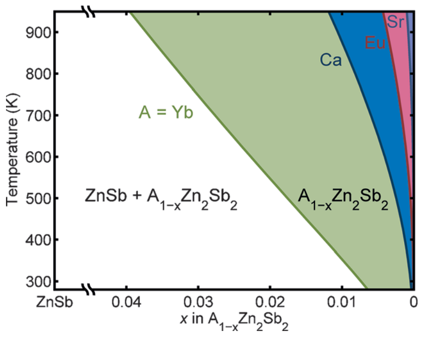
Inside Cover

Defects in Zintl Compounds

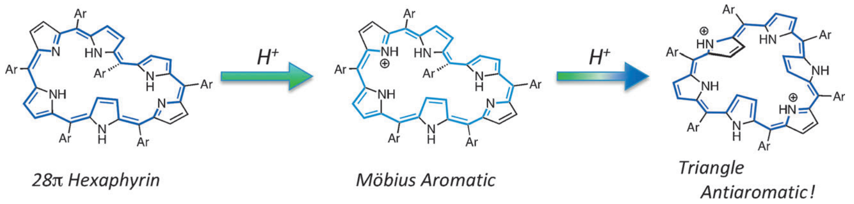
G. S. Pomrehn, A. Zevalkink, W. G. Zeier, A. van de Walle, G. J. Snyder* **3422 – 3426**

Defect-Controlled Electronic Properties in AZn_2Sb_2 Zintl Phases

Experimentally, AZn_2Sb_2 samples (A = Ca, Sr, Eu, Yb) are found to have large charge carrier concentrations that increase with increasing electronegativity of A. DFT calculations now confirm that the defect energies of A-site vacancies follow the same trend, suggesting that cation vacancies are the primary mechanism responsible for varying the carrier concentration in nominally valence-precise AZn_2Sb_2 compounds.

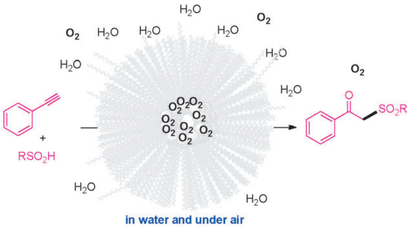


Porphyrinoids



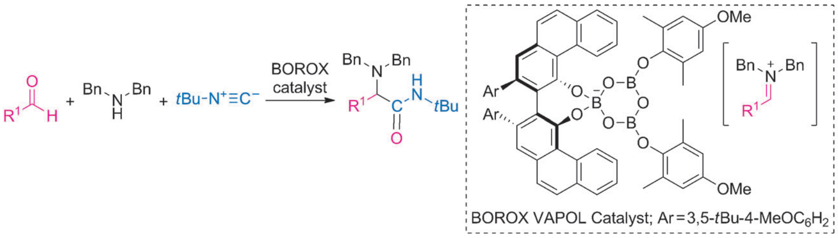
Protonation of [28]hexaphyrins(1.1.1.1.1.1) triggers conformational changes. Whereas protonation with trifluoroacetic acid leads to the formation of monoprotonated Möbius aromatic species, protonation with methanesulfonic acid leads to the formation of diprotonated triangular antiaromatic species. A peripherally hexaphenylated [28]hexaphyrin was rationally designed to undergo diprotonation to afford a triangular-shaped antiaromatic species.

Micellar Reactions



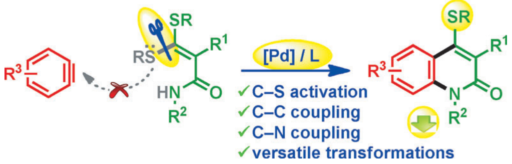
It's all happenin' in the micelle! The highly preferential dissolution of oxygen gas within the lipophilic cores inside nanomicelles leads to efficient trapping of in situ generated vinyl radicals. These intermediate radicals, derived from arylalkynes and sulfinic acids, lead to β-ketosulfone products, formed under especially mild and green conditions: no metals, no heating or cooling, recyclable aqueous media, and low E Factors.

Asymmetric Catalysis



Harmonious arrangement of parts: A screen of BOROX catalysts that were generated in situ from 13 different ligands and 47 alcohols led to the identification of an effective combination for the catalytic asymmetric three-component Ugi reaction. Experimental results suggest that the catalyst is a chiral polyborate anion, which then forms an ion pair with the iminium cation that is generated from aldehyde and secondary amine.

Synthetic Methods

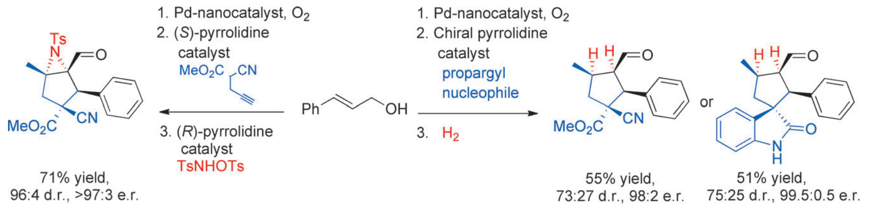


Within range: Under palladium catalysis a wide range of α-carbamoyl ketene dithioacetals readily react with arynes to selectively afford 2-quinolinones in high yields under neutral reaction conditions by the title sequence (see scheme). An attractive feature of the new strategy also lies in the versatile transformations of the alkylthio-substituted quinolinones.

Synthetic Methods

L. Deiana, Y. Jiang, C. Palo-Nieto,
S. Afewerki, C. A. Incerti-Pradillos,
O. Verho, C.-W. Tai, E. V. Johnston,*
A. Córdova* ———— **3447 – 3451**

Combined Heterogeneous Metal/Chiral Amine: Multiple Relay Catalysis for Versatile Eco-Friendly Synthesis

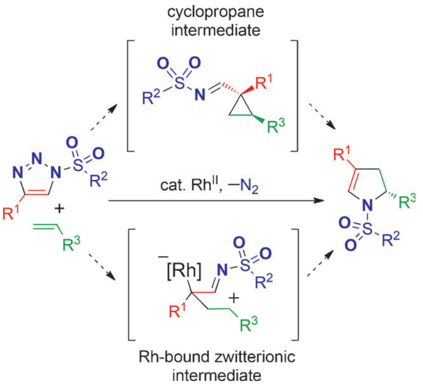


Relay switch: A versatile strategy for expansion of chemical space and the synthesis of valuable molecules, having up to three quaternary stereocenters, in a highly enantioselective fashion from simple alcohols is described. The method employs integrated heterogeneous metal/chiral amine multiple relay catalysis and air/O_2 as the terminal oxidant.

Azavinyl Carbenes

S. W. Kwok, L. Zhang, N. P. Grimster,
V. V. Fokin* ———— **3452 – 3456**

Catalytic Asymmetric Transannulation of NH-1,2,3-Triazoles with Olefins



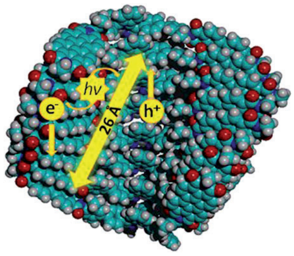
Enantioenriched dihydropyrroles can be generated by a rhodium(II)-catalyzed asymmetric transannulation between sulfonyl-1,2,3-triazoles and electron-rich styrenes. Mechanistic investigations support the formation of cyclopropane intermediates which undergo ring expansion to 2,3-dihydropyrroles in the presence of a chiral Brønsted acid catalyst.

Self-Assembled Charge Conduits

V. V. Roznyatovskiy, R. Carmieli,
S. M. Dyar, K. E. Brown,
M. R. Wasielewski* ———— **3457 – 3461**

Photodriven Charge Separation and Transport in Self-Assembled Zinc Tetrabenzotetraphenylporphyrin and Perylenediimide Charge Conduits

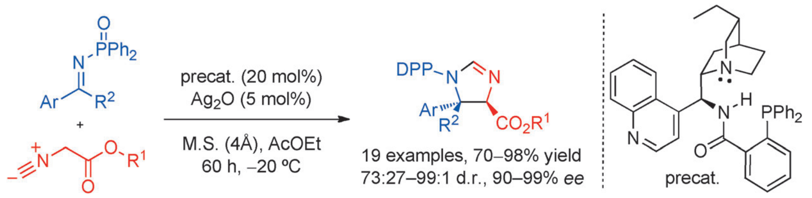
Zinc tetrabenzotetraphenylporphyrin (ZnTBTPP) covalently attached to four perylenediimide (PDI) acceptors self-assembles into a π-stacked, segregated columnar structure. Photoexcitation of ZnTBTPP rapidly produces a long-lived electron–hole pair with a 26 Å average separation distance, which is much longer than if the pair is confined within the covalent monomer. The charges are thus mobile within their respective segregated ZnTBTPP and PDI charge conduits.



Asymmetric Synthesis

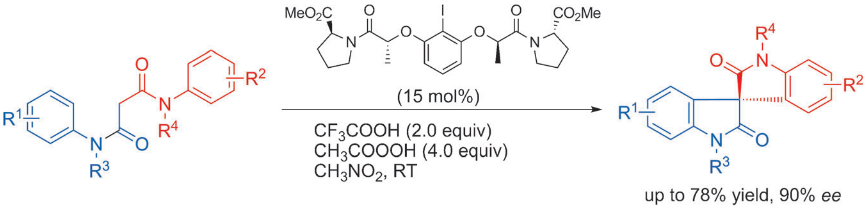
I. Ortín, D. J. Dixon* ———— **3462 – 3465**

Direct Catalytic Enantio- and Diastereoselective Mannich Reaction of Isocyanoacetates and Ketimines



Binary catalyst system: A catalytic asymmetric synthesis of imidazolines with a fully substituted β-carbon atom through a Mannich-type addition/cyclization reaction of isocyanoacetate pronucleophiles and N-diphenylphosphinoyl ketimines has been developed. By employing a cinchona-derived aminophosphine precatalyst and silver oxide as a binary catalyst system, good reactivity and high diastereo- and enantioselectivities were obtained.

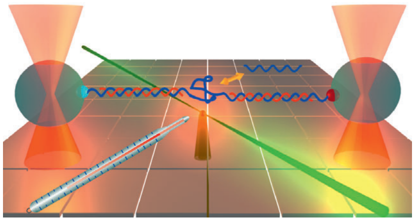
C–H Functionalization



'I' on the ball: The title oxidative coupling reaction of N^1,N^3-diphenylmalonamides has been established by using chiral organoiodine compounds as catalysts. Four C–H bonds were stereoselectively functionalized to give spirooxindoles with high levels of enantioselectivity.

Single-Molecule Thermometry

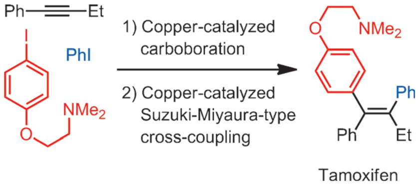
Back Cover



T-Jump: A simple and generic temperature control system is capable of achieving a large-scale temperature jump within milliseconds by focusing low-intensity lasers on black microparticles. The mechanochemical properties of a single molecule, such as a DNA hairpin molecule, are exploited to measure the temperature in a yoctoliter volume in real time.

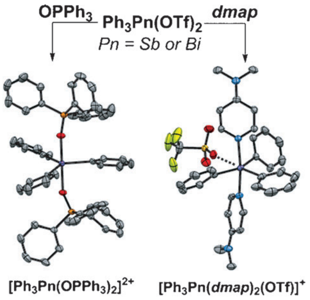
Cross-Coupling

Cross-Cu-pling: The title cross-couplings function well with a variety of substituted aryl iodides and aryl boronic esters and allows for reactivity orthogonal to that of the palladium-catalyzed processes. The title carboboration method includes both alkynes and allenes and provides access to highly substituted and stereodefined vinyl boronic esters. The alkyne carboboration method is highlighted in a simple one-pot synthesis of Tamoxifen.



Main-Group Elements

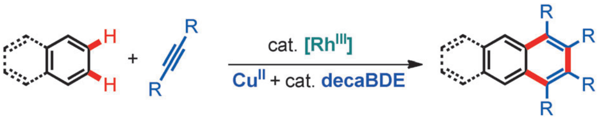
A coordinated effort: The synthesis and characterization of $OPPh_3$, dmap (4-(dimethylamino)pyridine), and bipy (2,2′-bipyridine) complexes of Sb^V and Bi^V are reported. The solid-state structures demonstrate structural diversity driven by the steric demands and the nature of the ligands.



C–H Activation

M. V. Pham, N. Cramer* ____ **3484 – 3487**

Aromatic Homologation by Non-Chelate-Assisted Rh^{III}-Catalyzed C–H Functionalization of Arenes with Alkynes

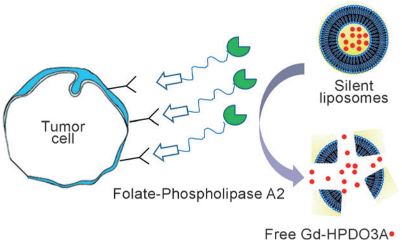


Multi-ring circus: The aromatic homologation of unfunctionalized, directing-group-free arenes with internal alkynes is promoted by a rhodium(III) catalyst in conjugation with suitable oxidants. The method tolerates a variety of functional groups and delivers highly substituted and highly soluble condensed arenes. These products provide access to acene structures with important electronic and photophysical properties.

Analytical Methods

D. Alberti, M. van't Erve, R. Stefania,
M. R. Ruggiero, M. Tapparo,
S. Geninatti Crich,* S. Aime **3488 – 3491**

A Quantitative Relaxometric Version of the ELISA Test for the Measurement of Cell Surface Biomarkers

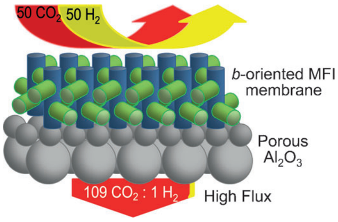


Personalized medicine: Translation of personalized medicine from the laboratory into the clinic requires the development of new sensitive and quantitative methods for the measurements of clinically relevant markers. A new NMR method (R-ELISA) has been used to detect the folate receptor on human ovarian cancer cells (see picture) using a phospholipase that is able to induce the release of paramagnetic species from liposomes.

Zeolite Materials

M. Zhou,* D. Korelskiy, P. Ye, M. Grahn,
J. Hedlund ____ **3492 – 3495**

A Uniformly Oriented MFI Membrane for Improved CO_2 Separation

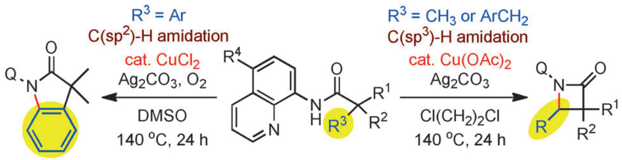


Porous chorus: An MFI membrane with a uniform *b*-axis orientation and 0.5 μm thick was prepared by the growth of an MFI monolayer in a tetrapropylammonium fluoride gel on a porous alumina substrate. The MFI membrane has a CO_2/H_2 separation selectivity of 109 and a CO_2 permeance of $51 \times 10^{-7}\ mol\,m^{-2}\,s^{-1}\,Pa^{-1}$; it separated a CO_2/H_2 mixture at a feed pressure of 9 bar and no sweep gas was used.

C–H Activation

Z. Wang, J. Ni, Y. Kuninobu,*
M. Kanai* ____ **3496 – 3499**

Copper-Catalyzed Intramolecular $C(sp^3)$–H and $C(sp^2)$–H Amidation by Oxidative Cyclization

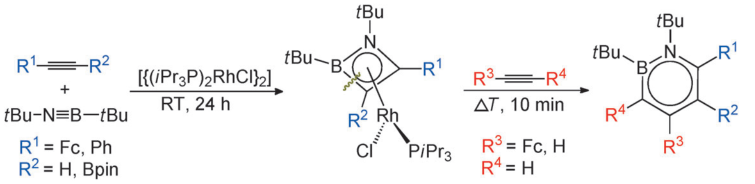


Silver ox: By using a $Cu(OAc)_2$ catalyst and an Ag_2CO_3 oxidant in dichloroethane solvent, $C(sp^3)$–H amidation proceeded at a terminal methyl group as well as at the internal benzylic position of an alkyl chain. This reaction has a broad substrate scope, and various β-lactams were obtained in excellent yield, even on a gram scale. Use of $CuCl_2$ and Ag_2CO_3 under an O_2 atmosphere led to 2-indolinone selectively synthesized by $C(sp^2)$–H amidation. DMSO = dimethylsulfoxide.

BN Heterocycles

H. Braunschweig,* K. Geetharani,
J. O. C. Jimenez-Halla,
M. Schäfer ______ 3500 – 3504

Direct Synthetic Route to Functionalized 1,2-Azaborinines

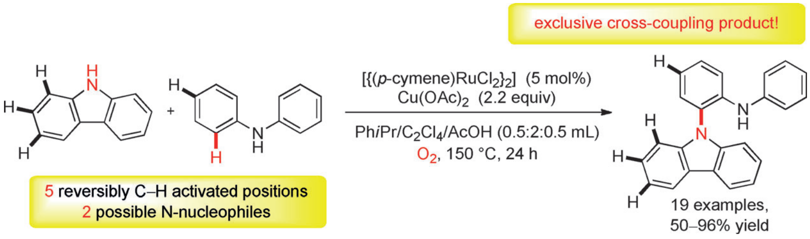


2+2+2: A straightforward method to access the first examples of ferrocene- and pinacolatoborane-functionalized 1,2-azaborinine derivatives has been developed by the tandem [2+2]/[2+4] cycloaddition reactions of di-*tert*-butyliminoboranes and alkynes.

Dehydrogenative C–N Cross-Coupling

M.-L. Louillat, A. Biafora, F. Legros,
F. W. Patureau* ______ 3505 – 3509

Ruthenium-Catalyzed Cross-Dehydrogenative *ortho*-N-Carbazolation of Diarylamines: Versatile Access to Unsymmetrical Diamines



No–No–No: Amination of a **no**n-acidic C–H bond, **no** pre-activation of the coupling partners, **no** chelate-assisting directing group. Dehydrogenative C–N cross-coupling through the *ortho*-N-carbazolation of unprotected, secondary anilines has been achieved using a Ru catalyst with O_2 as the terminal oxidant. The reactions proceed in an intermolecular fashion, selectively in the *ortho* position.

DOI: 10.1002/anie.201401096

Flashback: 50 Years Ago …

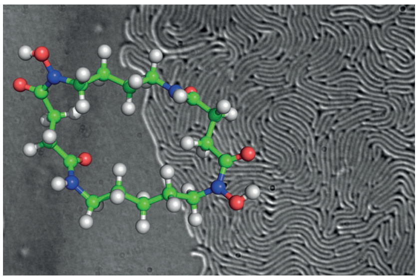
Unsaturated fatty acids was the topic of a Review by L. D. Bergelson and M. M. Shemyakin, who described how carbonyl olefination reactions can be sterically controlled to produce either *cis* or *trans* olefins. The topic of saturated and unsaturated fatty acids, in particular *trans* fatty acids, is still very much in the foreground today (for a recent Essay see *Angew. Chem. Int. Ed.* **2013**, *52*, 5220).

M. Schlosser (see *Angew. Chem. Int. Ed.* **2013**, *52*, 12483 for his Obituary) started a series of Reviews on organosodium and organopotassium compounds (such as phenylsodium or benzylpotassium). This first instalment concentrated on the properties, synthesis, and reactions of these compounds, including replacement of the metal and rearrangements.

In the Communications section, F. Jellinek et al. reported the first synthesis of allylbis(cyclopentadienyl)titanium(III), which involved the reaction of $[(C_5H_5)_2Ti^{IV}Cl_2]$ and allyl Grignard reagents to form the product as purple crystals. G. Scheibe et al. used proton NMR measurements to investigate internal rotation in cyanine dyes. The NMR spectra of *N*,*N*-dimethyl-substituted dyes showed two signals of equal intensity for the two methyl groups, thus confirming that internal rotation is hindered.

Read more in Issue 4/1964.

Going for the iron: The compound avaroferrin produced by *Shewanella* is a potent inhibitor of *Vibrio* swarming. Avaroferrin stops the swarming without killing the *Vibrio* bacteria by preventing iron piracy.

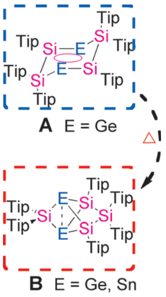


Bacterial Swarms

T. Böttcher, J. Clardy* ——— **3510–3513**

A Chimeric Siderophore Halts Swarming *Vibrio*

Heavy benzenes: The reduction of the product from disilenide and $GeCl_2$·dioxane or $SnCl_2$·dioxane, respectively, gives Ge- and Sn-containing heavier isomers of benzene. With Ge, the dismutational isomer of a 1,4-digermatetrasilabenzene (**A**; Tip = 2,4,6-$iPr_3C_6H_2$) is formed. Thermal rearrangement gives the presumed global minimum isomer **B**. With Sn, **B** is formed directly. Unprecedented downfield shifts in the ^{29}Si NMR spectra are rationalized by paramagnetic shielding-term contributions.



Aromatic Group 14 Compounds

A. Jana, V. Huch, M. Repisky,
R. J. F. Berger,*
D. Scheschkewitz* ——— **3514–3518**

Dismutational and Global-Minimum Isomers of Heavier 1,4-Dimetallatetrasilabenzenes of Group 14

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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