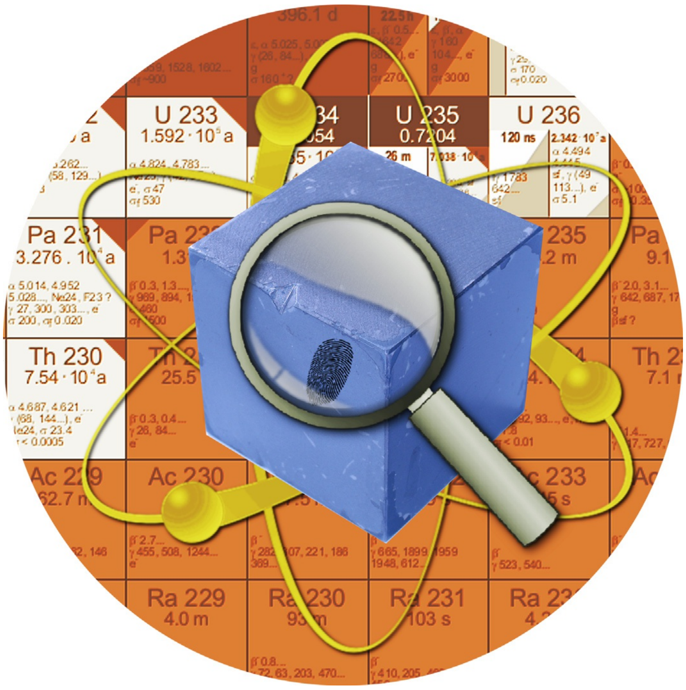
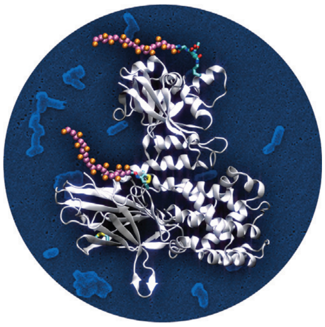
Nuclear forensics ...



… was used to trace the history of two pieces of uranium metal, which are purported to originate from the first German nuclear reaction experiments in the 1940s. In their Communication on page 13452 ff., M. Wallenius et al. compared the macroscopic sample properties with literature information and determined the production date and source of the uranium samples.

Glycoproteins

In their Communication on page 13198 ff., Q.-Y. Hu, F. Micoli et al. present two methods for the preparation of glycoconjugate vaccines with one single sugar chain linked to one or two positions of a carrier protein.

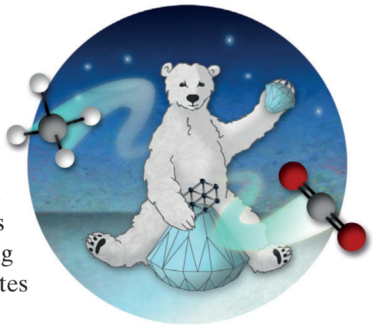


Programmable Materials

A. Walther et al. describe in their Communication on page 13258 ff. how the autonomous self-regulation of a pH-responsive peptide hydrogelator by internal biocatalytic feedback results in dynamic hydrogels.

High-Pressure Phases

In their Communication on page 13332 ff., S. A. Moggach et al. explore the gas uptake of porous MOFs by using gases as pressure-transmitting media. A study with supercritical CH_4 demonstrates two high-pressure phase transitions.



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Author Profile

"My favorite author (fiction) is Douglas Adams. My favorite types of music are Alternative, Indie and Classic Rock …"
This and more about Ralf Haiges can be found on page 13162.

News

T. Lindahl

P. Modrich

A. Sancar

Nobel Prizes 2015

Books

Highlights

GPCRs

D. Möller, P. Gmeiner* **13166 – 13168**

Arrestin-Bound Rhodopsin: A Molecular Structure and its Impact on the Development of Biased GPCR Ligands

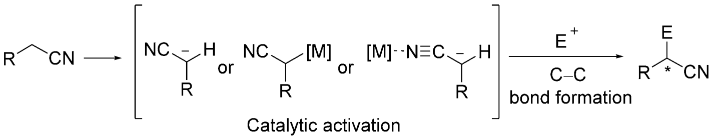
Freeze, you're under arrest: Serial femtosecond crystallography was used to solve the first high-resolution structure of the G-protein-coupled receptor rhodopsin bound to the adaptor protein arrestin. This template may be useful for the structure-based design of functionally selective drugs.

Minireviews

Synthetic Methods

R. López, C. Palomo* **13170 – 13184**

Cyanoalkylation: Alkylnitriles in Catalytic C–C Bond-Forming Reactions



On the playlist: This review provides an overview on the catalytic activation modes employed to overcome the attenuated reactivity of alkylnitriles as carbon pronucleophiles in catalytic carbon–carbon bond-forming reactions. The lack of catalytic asymmetric procedures clearly poses a challenge and offers a great opportunity for future improvements in this emerging area of research.

Reviews

Renewable Feedstock

J.-P. Lange* **13186 – 13197**

Renewable Feedstocks: The Problem of Catalyst Deactivation and its Mitigation

Rising to the challenge: This Review focuses on the main challenges concerning the long-term stability of catalysts for the conversion of bio-based feedstock into fuels and chemicals. Methods have been proposed to achieve this goal. Three main challenges need to be overcome to solve the problem of catalyst deactivation: catalyst fouling, catalyst poisoning, and catalyst destruction.

For the USA and Canada:
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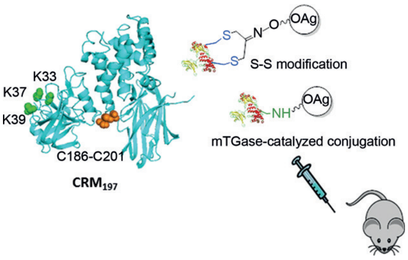
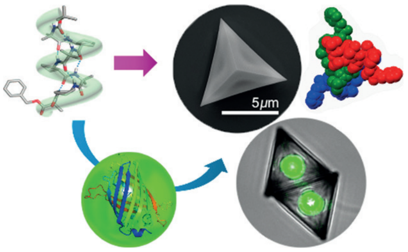
Communications



A vaccine against salmonella: Two methods are reported for the preparation of site-selective glycoconjugate vaccines with one single sugar chain linked to one or two precise positions of the CRM_{197} carrier protein (see picture; OAg = O-Antigen). The point of linkage on the protein plays a role in determining the immunogenicity of the glycoconjugate vaccines in mice.

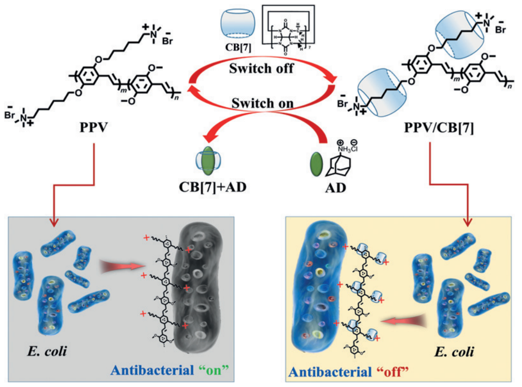
Glycoproteins

Frontispiece



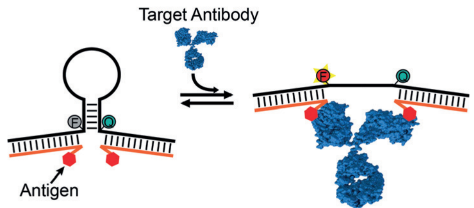
Gigantic molecular containers: The self-assembly of an 11-helical foldamer provided highly crystalline, hollow foldectures with truncated trigonal bipyramid shape. These foldectures are molecular hosts in a way reminiscent of a biological microcompartment.

Foldamers



A supramolecular antibiotic switch to reversibly "turn-on" and "turn-off" antibacterial activity on demand was developed as a proof-of-concept to regulate antibacterial activity. The switch relies on the supramolecular assembly and disassembly of a poly(phenylene vinylene) derivative (PPV) with cucurbit[7]uril (CB[7]). This strategy does not require any chemical modification on the active sites of the antibacterial agent.

Antibiotic Switches



A versatile system for the one-step fluorescence detection of proteins is based on a conformation-switching stem–loop DNA scaffold that presents a recognition element on each of its two stem strands. The steric strain associated with the binding of target molecules opens the stem, thus enhancing the emission of an attached fluorophore/quencher pair.

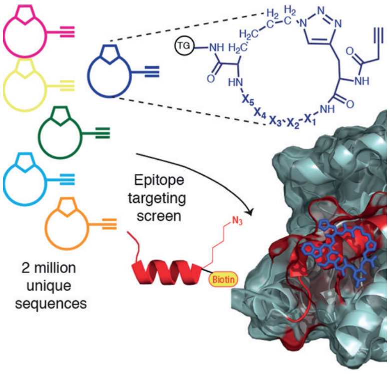
Biosensors

Combinatorial Chemistry

S. Das, A. Nag, J. Liang, D. N. Bunck, A. Umeda, B. Farrow, M. B. Coppock, D. A. Sarkes, A. S. Finch, H. D. Agnew, S. Pitram, B. Lai, M. B. Yu, A. K. Museth, K. M. Deyle, B. Lepe, F. P. Rodriguez-Rivera, A. McCarthy, B. Alvarez-Villalonga, A. Chen, J. Heath, D. N. Stratis-Cullum, J. R. Heath* ———— **13219 – 13224**

A General Synthetic Approach for Designing Epitope Targeted Macrocyclic Peptide Ligands

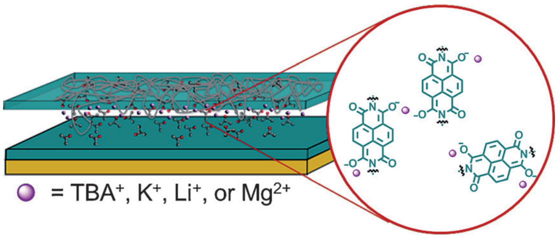
Match made in situ: 12 peptide ligands against distinct epitopes of challenging proteins were developed using a general strategy. A synthetic epitope with an azide was screened against an alkyne-containing macrocyclic library to identify the best binder. These macrocyclic ligands can enable antibody-like therapeutic and diagnostic applications, with small molecular footprints.



Electrical Energy Storage

C. R. DeBlase, K. Hernández-Burgos, J. M. Rotter, D. J. Fortman, D. S. Abreu, R. A. Timm, I. C. N. Diógenes, L. T. Kubota, H. D. Abruña,* W. R. Dichtel* ———— **13225 – 13229**

Cation-Dependent Stabilization of Electrogenerated Naphthalene Diimide Dianions in Porous Polymer Thin Films and Their Application to Electrical Energy Storage

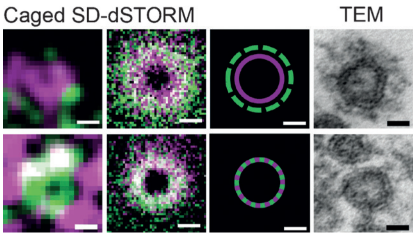


Charge me up: Thin films of a naphthalene diimide porous polymer exhibit 20% greater energy density in the presence of counter cations that stabilize their reduced forms in the solid-state. Such behaviour is not observed for the monomer in solution, pointing to the importance of polymer structure in electrical energy storage devices.

Single-Molecule Microscopy

M. Lehmann,* B. Gottschalk, D. Puchkov, P. Schmieder, S. Schwagerus, C. P. R. Hackenberger, V. Haucke, J. Schmoranzer* ———— **13230 – 13235**

Multicolor Caged dSTORM Resolves the Ultrastructure of Synaptic Vesicles in the Brain

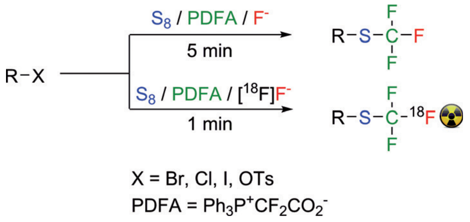


dSTORM gets colorful: A screen for fluorescence recovery following reduction revealed several dyes suitable for high-resolution caged dSTORM imaging. Using dye pairs, multicolor localization precision could be achieved below 15 nm. This system is used to resolve the ultrastructure of single synaptic vesicles. Scale bar: 20 nm.

Carbenes

J. Zheng, L. Wang, J.-H. Lin, J.-C. Xiao,* S. H. Liang* ———— **13236 – 13240**

Difluorocarbene-Derived Trifluoromethylthiolation and [^{18}F]Trifluoromethylthiolation of Aliphatic Electrophiles

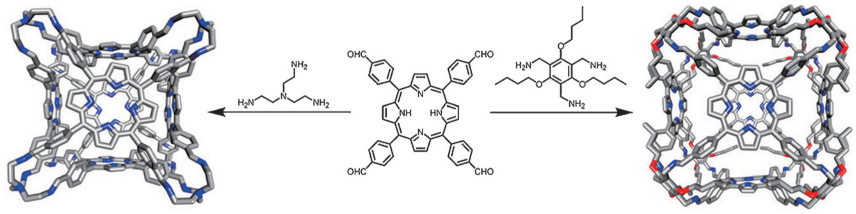


[^{18}F] label: An efficient, fast, and transition-metal-free protocol for trifluoromethylthiolation of alkyl electrophiles with in situ generated difluorocarbene in the presence of elemental sulfur and external fluoride ions is described. This strategy was applied to [^{18}F]trifluoromethylthiolation of alkyl electrophiles, which represents the first example of this type. Ts = 4-toluenesulfonyl.

Organic Cages

S. Hong, M. R. Rohman, J. Jia, Y. Kim, D. Moon, Y. Kim, Y. H. Ko, E. Lee, K. Kim* ________ **13241 – 13244**

Porphyrin Boxes: Rationally Designed Porous Organic Cages

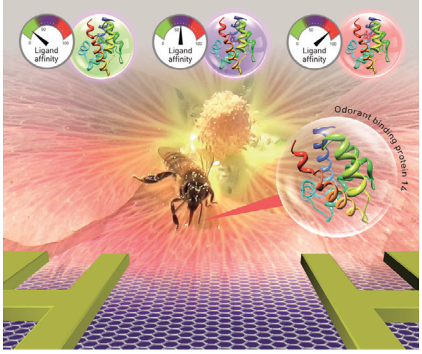


Find a way: A new strategy for synthesis of shape-persistent organic cages based on porphyrins through rational design is reported. The size of cavities and windows of the organic cages can be modulated using different sized building units while maintaining the topology of the cages.

Biosensors

M. Larisika, C. Kotlowski, C. Steininger, R. Mastrogiacomo, P. Pelosi, S. Schütz, S. F. Peteu, C. Kleber, C. Reiner-Rozman, C. Nowak, W. Knoll* ____ **13245 – 13248**

Electronic Olfactory Sensor Based on *A. mellifera* Odorant-Binding Protein 14 on a Reduced Graphene Oxide Field-Effect Transistor

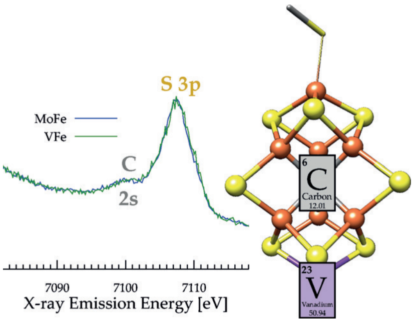


Smell checker: Olfaction of the honey bee was mimicked by a graphene-based biosensor. Electrical measurements monitored the binding of honey-bee-attracting odorants to the immobilized receptor odorant-binding protein 14 (OBP14). The sensor is able to discriminate between odorants in real time in a quantitative manner, yielding full reaction kinetics of ligand–receptor interactions, and revealed the importance of a hydroxy substituent for the recognition of aromatic odorants.

Nitrogenases

J. A. Rees, R. Bjornsson, J. Schlesier, D. Sippel, O. Einsle, S. DeBeer* ________ **13249 – 13252**

The Fe–V Cofactor of Vanadium Nitrogenase Contains an Interstitial Carbon Atom

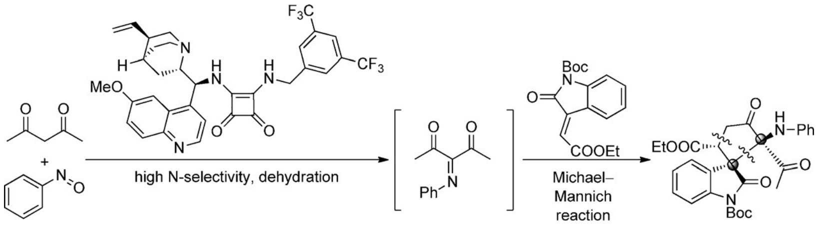


Stuck in the middle: The first experimental evidence for the presence of an interstitial carbide in the active-site Fe–V cofactor in vanadium nitrogenase is presented. The presence of the carbide was identified using valence-to-core X-ray emission spectroscopy. The carbide is analogous to that of the Fe–Mo cofactor of molybdenum nitrogenase, and is only the second reported carbide ligand in biology.

Organocatalysis

Q.-S. Sun, H. Zhu, Y.-J. Chen, X.-D. Yang, X.-W. Sun,* G.-Q. Lin ____ **13253 – 13257**

Squaramide-Catalyzed Synthesis of Enantioenriched Spirocyclic Oxindoles via Ketimine Intermediates with Multiple Active Sites



Five-membered spirocyclic oxindoles are generated in excellent yields (up to 94 %) and stereoselectivities (up to > 20:1 d.r., > 99 % *ee*) in a Michael–Mannich reaction of a ketimine intermediate that is catalyzed by a bifunctional quinine-derived squaramide. A scaled-up variant of this transformation also proceeded smoothly, highlighting the potential of this cascade process.

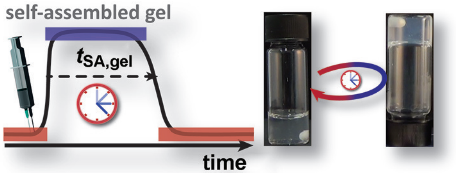
Inside Cover

Programmable Materials

T. Heuser, E. Weyandt,
A. Walther* ______ **13258 – 13262**

Biocatalytic Feedback-Driven Temporal Programming of Self-Regulating Peptide Hydrogels

Inside Back Cover



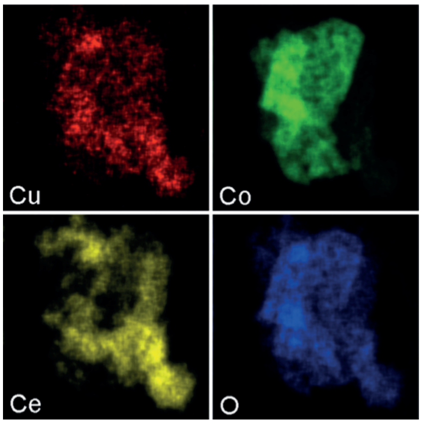
Programmed to self-destruct: An internal enzymatic feedback system enables the autonomous self-regulation over time of a pH-responsive peptide gelator (see picture; SA = self-assembly). The resulting dynamic hydrogels with programmed lifetimes are suitable for application in fluidic guidance, burst release, and transient rapid prototyping.

CO Oxidation

A. J. Binder,* T. J. Toops,* R. R. Unocic,
J. E. Parks, II, S. Dai* ______ **13263 – 13267**

Low-Temperature CO Oxidation over a Ternary Oxide Catalyst with High Resistance to Hydrocarbon Inhibition

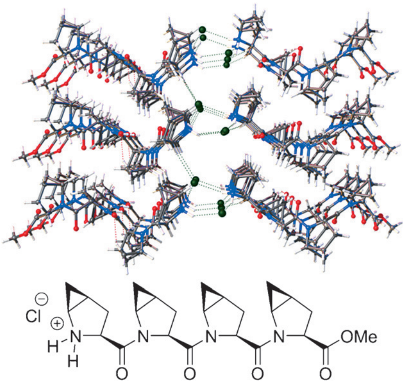
Cheaper and better: Platinum group metal (PGM) catalysts struggle with CO oxidation at low temperatures (< 200 °C) due to inhibition by hydrocarbons in exhaust streams. A ternary oxide composed of copper oxide, cobalt oxide, and ceria (CCC) is presented that outperforms commercial PGM catalysts for CO oxidation in simulated automotive exhaust streams while showing no signs of inhibition by propene.



Proline Isomerization

G. Berger, M. Vilchis-Reyes,
S. Hanessian* ______ **13268 – 13272**

Structural Properties and Stereochemically Distinct Folding Preferences of 4,5-*cis* and *trans*-Methano-L-Proline Oligomers: The Shortest Crystalline PPII-Type Helical Proline-Derived Tetramer



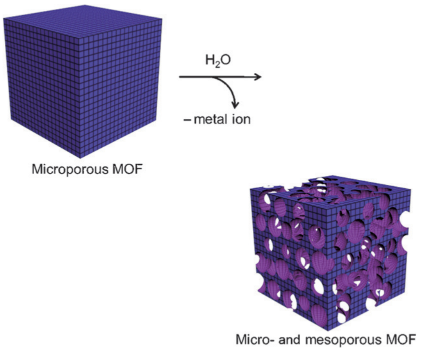
A crystalline PPII-type helical tetramer formed of *cis*-4,5-methano-L-proline is presented. X-ray diffraction and circular dichroism together with theoretical results highlight the differential behavior of *cis*- and *trans*-4,5-methano-L-proline oligomers. These proline methanologues could be incorporated in drugs and peptides as proline mimics with structurally tweaked properties.

Hierarchical Porous Materials

Y. Kim, T. Yang, G. Yun, M. B. Ghasemian,
J. Koo, E. Lee, S. J. Cho,
K. Kim* ______ **13273 – 13278**

Hydrolytic Transformation of Microporous Metal–Organic Frameworks to Hierarchical Micro- and Mesoporous MOFs

Micro- to mesoporous transformation: The microporous metal–organic framework POST-66(Y) was transformed into a hierarchical micro- and mesoporous MOF, POST-66(Y)-wt. The mesopores, with a diameter of 3–20 nm, are easily obtained by simple treatment of POST-66(Y) with water.

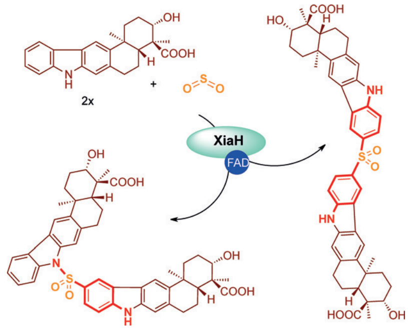


Sulfa Drugs

M. Baunach, L. Ding, K. Willing, C. Hertweck* ______ **13279 – 13283**

Bacterial Synthesis of Unusual Sulfonamide and Sulfone Antibiotics by Flavoenzyme-Mediated Sulfur Dioxide Capture

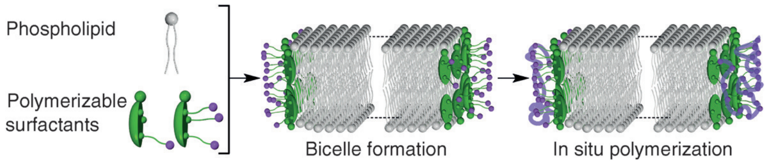
Ménage à trois: A radical-based, three-component reaction of xiamycin and sulfur dioxide leads to the biosynthesis of various bacterial sulfonamide and diarylsulfone antibiotics. Gene deletion, complementation, and biotransformation experiments unequivocally showed the involvement of the flavoprotein XiaH in the biosynthesis of these unprecedented sulfa compounds.



Model Membranes

R. Matsui, M. Ohtani, K. Yamada, T. Hikima, M. Takata, T. Nakamura, H. Koshino, Y. Ishida,* T. Aida ______ **13284 – 13288**

Chemically Locked Bicelles with High Thermal and Kinetic Stability

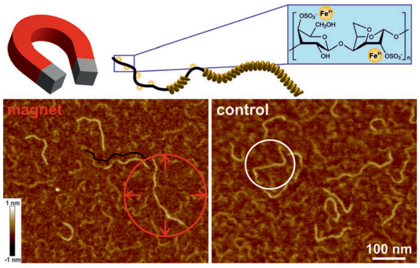


Link and lock: In situ polymerization of a bicellar mixture composed of a phospholipid and polymerizable surfactants afforded unprecedented stable bicelles. The polymerized composite showed an aligned phase over a wide thermal range with excellent ^{2}H quadrupole splitting of the solvent signal, thus suggesting utility as an alignment medium for NMR studies. The crosslinking also notably improved the kinetic stability and alignment morphology of the bicelles.

Conformation Analysis

L. Schefer, A. Bulant, C. Zeder, A. Saha, R. Mezzenga* ______ **13289 – 13292**

Magnetic Control of Macromolecular Conformations in Supramolecular Anionic Polysaccharide–Iron Complexes



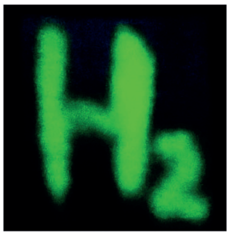
Enrichment of iota carrageenan polysaccharides with Fe^{2+} or Fe^{3+} induces a conformational transition from random coils to single helices. The noninvasive magnetic manipulation of individual iota–Fe^{II} macromolecular conformations is demonstrated by a magnetically induced stiffening and stretching of the helical chains. Multichain clusters arising from the efficient chelation of Fe^{3+} may serve for iron food fortification purposes.

Fluorescence Probes

VIP

P. Kos, H. Plenio* ______ **13293 – 13296**

A Fluorescent Molecular Probe for the Detection of Hydrogen Based on Oxidative Addition Reactions with Crabtree-Type Hydrogenation Catalysts

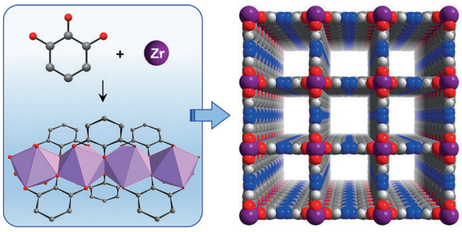


A green light for hydrogen: The oxidative addition of H$_2$ to a fluorophore-tagged Ir^{I} Crabtree-type complex leads to brightly fluorescent Ir^{III} dihydride species. This fluorogenic reaction is useful for sensing hydrogen and for uncovering mechanistic details in hydrogenation reactions.

Metal–Organic Frameworks

G. Mouchaham, L. Cooper, N. Guillou, C. Martineau, E. Elkaïm, S. Bourrelly, P. L. Llewellyn, C. Allain, G. Clavier, C. Serre, T. Devic* ——— **13297 – 13301**

A Robust Infinite Zirconium Phenolate Building Unit to Enhance the Chemical Stability of Zr MOFs

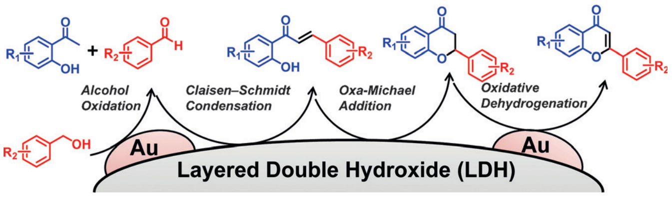


Water-proof MOF: The reaction of Zr^{IV} with 1,2,3-trioxobenzene moieties leads to the formation of a robust chain-like coordination motif. Such a motif is used to rationally build a new metal–organic framework (MOF) which combines a good water sorption capacity with high chemical stability in physiologically relevant conditions, outperforming archetypical Zr^{IV} carboxylate MOFs.

One-Pot Synthesis

T. Yatabe, X. Jin, K. Yamaguchi, N. Mizuno* ——— **13302 – 13306**

Gold Nanoparticles Supported on a Layered Double Hydroxide as Efficient Catalysts for the One-Pot Synthesis of Flavones



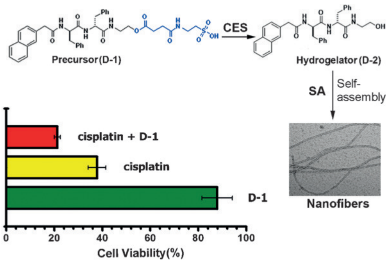
Go for gold: In the presence of gold nanoparticles supported on a Mg-Al layered double hydroxide (Au/LDH), various flavones were obtained from the corresponding 2′-hydroxyacetophenones and benzaldehydes (or benzyl alcohols). All three (four) steps of this one-pot process are catalyzed by Au/LDH in a truly heterogeneous fashion.

Prodrug Design

J. Li, Y. Kuang, J. Shi, J. Zhou, J. E. Medina, R. Zhou, D. Yuan, C. Yang, H. Wang, Z. Yang, J. F. Liu, D. M. Dinulescu,* B. Xu* ——— **13307 – 13311**

Enzyme-Instructed Intracellular Molecular Self-Assembly to Boost Activity of Cisplatin against Drug-Resistant Ovarian Cancer Cells

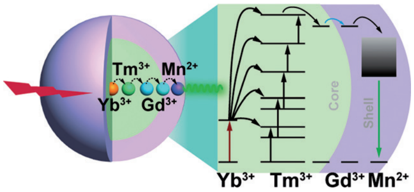
Cisplatin-boosting nanofibers: The design and synthesis is reported of small peptide precursors that can be cleaved by carboxylesterase (CES) to form peptides that self-assemble in water to form molecular nanofibers. The precursors themselves are innocuous to cells at optimal concentrations, but they double or triple the activity of cisplatin against drug-resistant ovarian cancer cells.



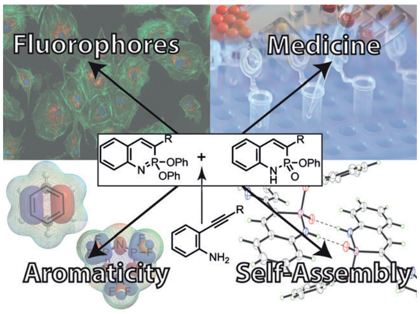
Core–Shell Nanostructures

X. Li, X. Liu, D. M. Chevrier, X. Qin, X. Xie, S. Song, H. Zhang,* P. Zhang,* X. Liu* ——— **13312 – 13317**

Energy Migration Upconversion in Manganese(II)-Doped Nanoparticles



On the up: The upconversion emission of Mn^{2+} ions can be realized in $NaGdF_4$:Yb/Tm@$NaGdF_4$:Mn core–shell nanoparticles by utilizing energy migration through the gadolinium sublattice (see figure). The multiphoton upconversion process can be further enhanced under pulsed laser excitation at high power densities. The ability of the Mn^{2+}-doped nanoparticles to easily undergo oxidization makes them attractive for use in hydrogen peroxide detection.



P–N on the scene: A simple route to the little explored phosphaquinoline scaffold is described. These heterocycles form strong homodimers in solution and the solid state, possess large Stokes shifts and high quantum yields at a range of emission wavelengths, and open the way to exploration of the delocalization within cycles containing $\mathrm{N{=}P^V}$ bonds.

Phosphorus Heterocycles

C. L. Vonnegut, A. M. Shonkwiler,
M. M. Khalifa, L. N. Zakharov,
D. W. Johnson,*
M. M. Haley* ——— **13318 – 13322**

Facile Synthesis and Properties of 2-λ^5-Phosphaquinolines and 2-λ^5-Phosphaquinolin-2-ones

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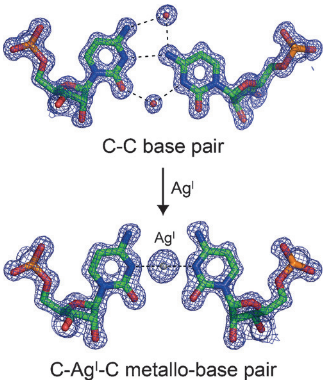

The high-resolution structures of C–Ag$^{\mathrm{I}}$–C base pairs in A-form RNA duplexes have been solved. Structural information on the present metallo-base pair together with the previously reported T–Hg$^{\mathrm{II}}$–T base pair widely open the possibility of structure-based design of nucleic-acid-based nanodevices containing the natural metallo-base pairs.

Noncanonical Metallo-Base Pairs

J. Kondo,* Y. Tada, T. Dairaku,
H. Saneyoshi, I. Okamoto, Y. Tanaka,
A. Ono ——— **13323 – 13326**

High-Resolution Crystal Structure of a Silver(I)–RNA Hybrid Duplex Containing Watson–Crick-like C–Silver(I)–C Metallo-Base Pairs

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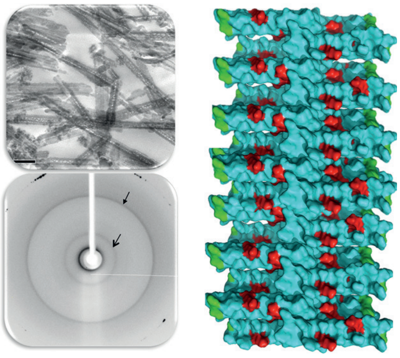
Nanowire Synthesis

Z. S. Al-Garawi, J. R. Thorpe,
L. C. Serpell* ______ 13327 – 13331

Silica Nanowires Templated by Amyloid-like Fibrils

Fibrillar peptide nanowire templates: Amyloid fibrils form silica nanowires with a peptidic core. By varying key residues within a known peptide sequence, lysine and arginine residues are shown to be necessary for templating the silica nanowire assembly.

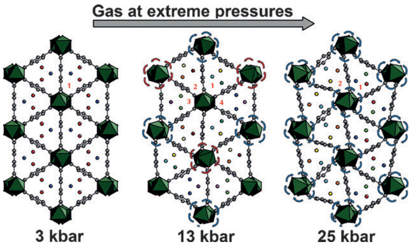


High-Pressure MOF Phases

J. Sotelo, C. H. Woodall, D. R. Allan,
E. Gregoryanz, R. T. Howie, K. V. Kamenev,
M. R. Probert, P. A. Wright,
S. A. Moggach* ______ 13332 – 13336

Locating Gases in Porous Materials: Cryogenic Loading of Fuel-Related Gases Into a Sc-based Metal–Organic Framework under Extreme Pressures

Back Cover

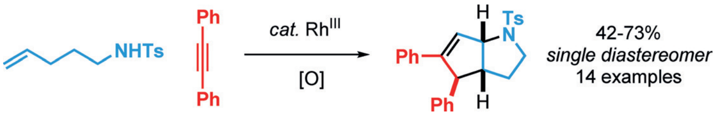


The maximum gas uptake of porous MOFs was explored by using gases as pressure-transmitting media in high-pressure single-crystal diffraction experiments. A study with supercritical CH_4 at 3–25 kbar demonstrates that two high-pressure phase transitions are induced as the filled MOF adapts to reduce the volume of the system.

C–H Bond Activation

A. Archambeau, T. Rovis* 13337 – 13340

Rhodium(III)-Catalyzed Allylic C(sp^3)–H Activation of Alkenyl Sulfonamides: Unexpected Formation of Azabicycles



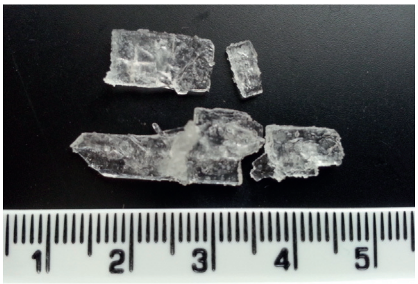
An unusual Rh-catalyzed C–H bond activation: Allylic C–H bond activation by a Rh^{III} catalyst precedes alkyne insertion leading to an unexpected azabicycle structure in good yield and excellent diastereoselectivity. The mechanism of the reaction was interrogated with deuterium-labeling experiments and is proposed to involve a 1,3-Rh shift followed by an electrocyclization event.

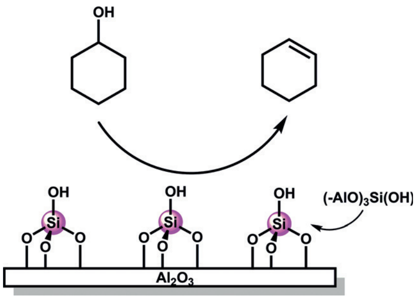
Oxidizing Agents

S. H. Ahn, K. J. Cluff, N. Bhuvanesh,
J. Blümel* ______ 13341 – 13345

Hydrogen Peroxide and Di(hydroperoxy)-propane Adducts of Phosphine Oxides as Stoichiometric and Soluble Oxidizing Agents

Hydrogen peroxide rocks! Di(hydroperoxy)propane adducts of phosphine oxides, $[R_3PO(HOO)_2CMe_2]$ (R = alkyl, aryl), are obtained as very large single crystals. Despite their oxidative power, the long-term stability of the compounds is high and they are very soluble in organic solvents. These compounds are therefore ideal oxidizing agents that can be applied stoichiometrically in nonaqueous media.





Strong enough to get the job done: By selectively installing isolated (-AlO)$_3$SiOH species on a γ-Al$_2$O$_3$ substrate, a unique "mild" Brønsted-acid catalytic site is formed. These well-defined sites evince highly uniform characteristics and are catalytically competent in the dehydration of cychohexanol, showing higher activity, no loss of selectivity, and no coking.

Heterogeneous Catalysis

A. R. Mouat, C. George, T. Kobayashi, M. Pruski, R. P. van Duyne, T. J. Marks,* P. C. Stair* ______ **13346 – 13351**

Highly Dispersed SiO$_x$/Al$_2$O$_3$ Catalysts Illuminate the Reactivity of Isolated Silanol Sites

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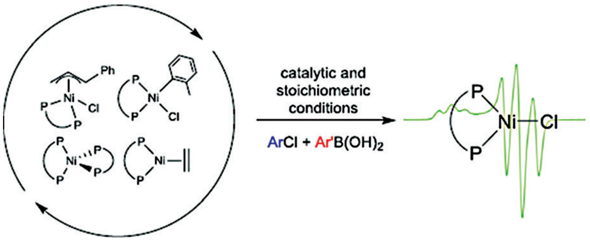
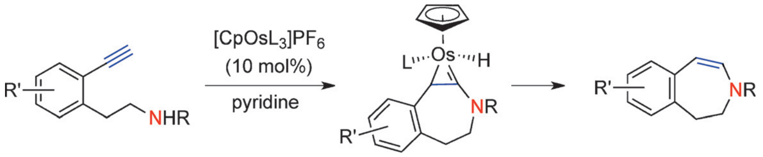


I and only I: A series of Ni^0, Ni^I and Ni^{II} complexes supported by a bidentate phosphine ligand were prepared. They are all active precatalysts for the Suzuki–Miyaura reaction, and generate an active Ni^I complex during catalysis. This observation led to the discovery of a bench-stable Ni^{II} compound, which can couple heterocylic substrates at room temperature.

Cross-Coupling

L. M. Guard, M. Mohadjer Beromi, G. W. Brudvig, N. Hazari,* D. J. Vinyard ______ **13352 – 13356**

Comparison of dppf-Supported Nickel Precatalysts for the Suzuki–Miyaura Reaction: The Observation and Activity of Nickel(I)



Capital catalysts: The osmium-catalyzed cyclization of *o*-alkynyl phenethylamines enabled the straightforward preparation of a broad range of dopaminergic 3-benzazepine derivatives. More commonly used metal catalysts did not promote the desired reaction efficiently. Mechanistic investigations revealed that the process takes place via osmacyclopropene intermediates, examples of which were isolated and characterized by X-ray diffraction analysis.

Heterocycle Synthesis

A. Álvarez-Pérez, C. González-Rodríguez, C. García-Yebra, J. A. Varela, E. Oñate, M. A. Esteruelas,* C. Saá* ______ **13357 – 13361**

Catalytic Cyclization of *o*-Alkynyl Phenethylamines via Osmacyclopropene Intermediates: Direct Access to Dopaminergic 3-Benzazepines

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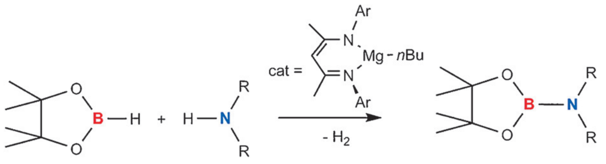


BoNd-forming catalysis: Dehydrocoupling reactions between the boranes HBpin and 9-borabicyclo[3.3.1]nonane, and a range of amines and anilines ensue under very mild reaction conditions in the presence of a simple β-diketiminato magnesium *n*-butyl precatalyst. The reaction is facilitated by the Lewis acidity of the borane substrate, and is dictated by resultant pre-equilibria between magnesium hydride and borohydride.

B–N Coupling

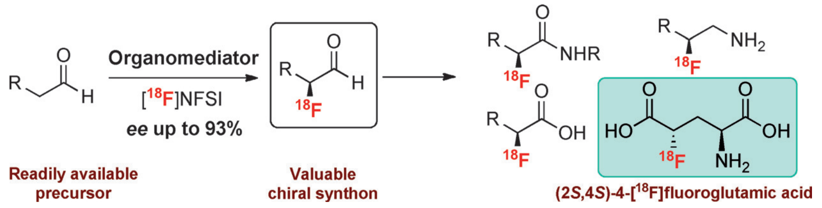
D. J. Liptrot, M. S. Hill,* M. F. Mahon, A. S. S. Wilson ______ **13362 – 13365**

Alkaline-Earth-Catalyzed Dehydrocoupling of Amines and Boranes

^{18}F Fluorination

F. Buckingham, A. K. Kirjavainen, S. Forsback, A. Krzyczmonik, T. Keller, I. M. Newington, M. Glaser, S. K. Luthra, O. Solin, V. Gouverneur* **13366 – 13369**

Organomediated Enantioselective ^{18}F Fluorination for PET Applications

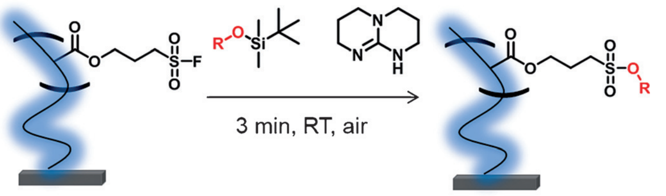


PET molecules: A metal-free asymmetric ^{18}F-labeling reaction for an aliphatic C–H bond, employing a chiral imidazolidinone as the organomediator and *N*-[^{18}F]fluorobenzenesulfonimide ([^{18}F]NFSI) as the ^{18}F source, is reported. The method is used to prepare the ^{18}F-labeled positron emission tomography (PET) radiotracer (2*S*,4*S*)-4-[^{18}F]fluoroglutamic acid.

Click Chemistry

J. Yatvin, K. Brooks, J. Locklin* ______________ **13370 – 13373**

SuFEx on the Surface: A Flexible Platform for Postpolymerization Modification of Polymer Brushes

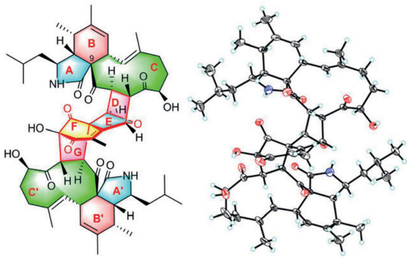


Sulfur(VI) fluoride exchange (SuFEx) is used to “click” a silyl ether rapidly and quantitatively to a polymer brush containing native SO_2F groups. SuFEx is further demonstrated to facilely add a variety of other functional groups to brush substrates, including alkynes, thiols, and dienes.

Natural Products

H. Zhu, C. Chen, Y. Xue, Q. Tong, X. N. Li, X. Chen, J. Wang, G. Yao, Z. Luo, Y. Zhang* ______________ **13374 – 13378**

Asperchalasine A, a Cytochalasan Dimer with an Unprecedented Decacyclic Ring System, from *Aspergillus flavipes*



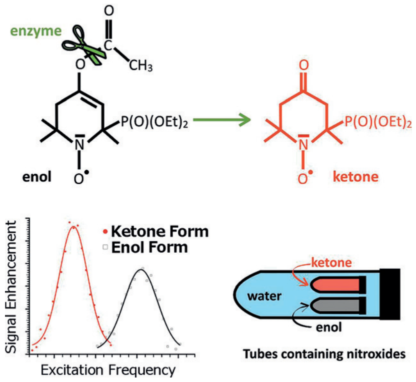
A complicated ring system: Asperchalasine A, the first cytochalasan dimer to possess a complex decacyclic 5/6/11/5/5/6/5/11/6/5 ring system, was isolated from *Aspergillus flavipes*, along with four biogenetic related intermediates, asperchalasines B–D. Asperchalasine A induced significant G1-phase cell cycle arrest in cancerous but not normal cells, highlighting it as a potentially selective cell cycle regulator against cancer cells.

In Vivo Imaging

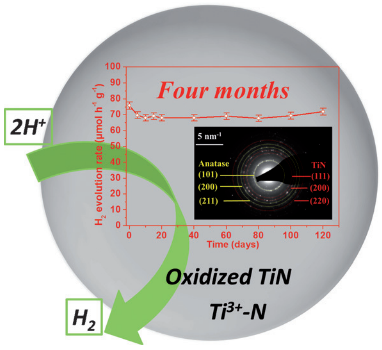
G. Audran,* L. Bosco, P. Brémond,* J.-M. Franconi, N. Koonjoo, S. R. A. Marque,* P. Massot, P. Mellet,* E. Parzy, E. Thiaudière* __ **13379 – 13384**

Enzymatically Shifting Nitroxides for EPR Spectroscopy and Overhauser-Enhanced Magnetic Resonance Imaging

Tautomers for in vivo protease imaging: Enzymatically activated nitroxides could be tracked by EPR and an Overhauser-enhanced MRI technique, permitting imaging of in vivo protease activity in the digestive tract of mice.



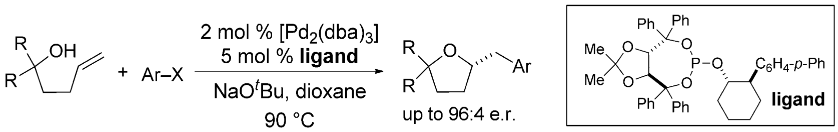
Thermal oxidization of TiN nanopowder can lead to an anatase phase of a photocatalyst capable of hydrogen evolution. The photocatalyst provides activity for hydrogen evolution under AM1.5 conditions, without the use of a noble metal cocatalyst, and is stable over extended periods of time.



Hydrogen Production

X. Zhou, E. M. Zolnhofer, N. T. Nguyen, N. Liu, K. Meyer, P. Schmuki* ———— 13385 – 13389

Stable Co-Catalyst-Free Photocatalytic H_2 Evolution From Oxidized Titanium Nitride Nanopowders

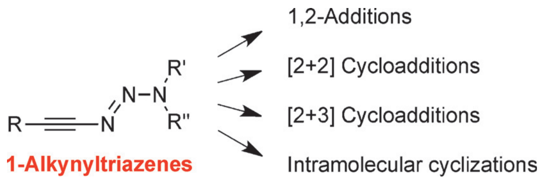


The construction of enantiomerically enriched tetrahydrofurans is accomplished by asymmetric Pd-catalyzed cross-coupling reactions between γ-hydroxyalkenes and aryl bromides. Use of a palladium catalyst supported by a new TADDOL-derived chiral phosphite ligand provides the tetrahydrofuran products in good yield with up to 96:4 e.r. (see scheme).

Asymmetric Catalysis

B. A. Hopkins, Z. J. Garlets, J. P. Wolfe* ———— 13390 – 13392

Development of Enantioselective Palladium-Catalyzed Alkene Carboalkoxylation Reactions for the Synthesis of Tetrahydrofurans

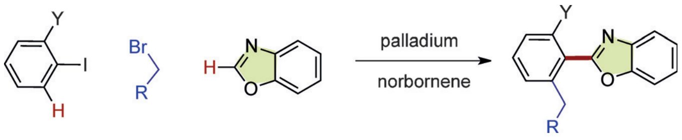


Cut from the same cloth: 1-Alkynyltriazenes are activated alkynes with a reactivity profile similar to ynamides. A series of different reactions are employed to compare the reactivities of the two compound classes. The triazene functional group in the products facilitates unique subsequent transformations.

Activated Alkynes

F. G. Perrin, G. Kiefer, L. Jeanbourquin, S. Racine, D. Perrotta, J. Waser, R. Scopelliti, K. Severin* – 13393 – 13396

1-Alkynyltriazenes as Functional Analogues of Ynamides



Three-in-one: The heteroarylation of aryl iodides and *ortho*-alkylation of the aryl rings occur in a single operation. The palladium and norbornene cocatalyst system effectively promoted the cleavage of two C–H bonds and the formation of two new C–C bonds, including a very hindered aryl–heteroaryl bond.

Heterocycles

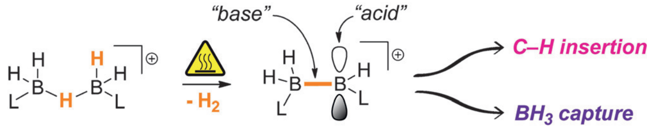
C. Lei, X. Jin, J. Zhou* —— 13397 – 13400

Palladium-Catalyzed Heteroarylation and Concomitant *ortho*-Alkylation of Aryl Iodides

C–H Activation

A. Prokofjevs* ________ **13401 – 13405**

Thermal Dehydrogenation of Base-Stabilized $B_2H_5^+$ Complexes and Its Role in C–H Borylation

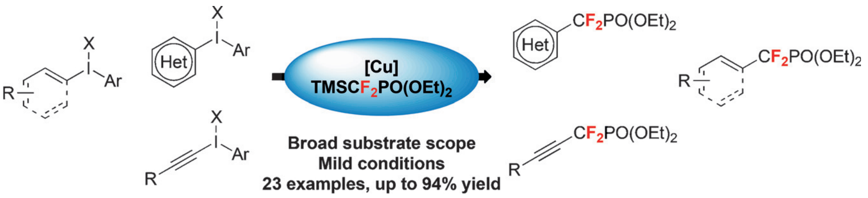


Catlike: In situ formation of a cationic sp^2–sp^3 diborane(4) is proposed to be the key step in the high-temperature intramolecular C–H borylation of amine boranes activated with catalytic amounts of strong electrophiles. Reaction mechanisms are discussed.

Synthetic Methods

M. V. Ivanova, A. Bayle, T. Besset,
T. Poisson,*
X. Pannecoucke ________ **13406 – 13410**

Copper-Mediated Formation of Aryl, Heteroaryl, Vinyl and Alkynyl Difluoromethylphosphonates: A General Approach to Fluorinated Phosphate Mimics

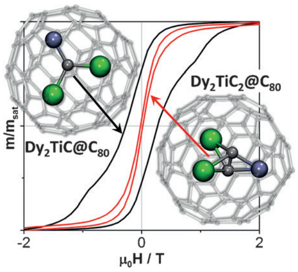


A general approach to aryl, heteroaryl, vinyl, and alkynyl difluoromethylphosphonates was developed providing access to a broad range of products including biologically relevant molecules in good to excellent yields. Mechanistic studies suggest the involvement of a copper(III) species as key intermediate.

Edohedral Fullerenes

K. Junghans, C. Schlesier, A. Kostanyan,
N. A. Samoylova, Q. Deng,
M. Rosenkranz, S. Schiemenz,
R. Westerström, T. Greber, B. Büchner,
A. A. Popov* ________ **13411 – 13415**

Methane as a Selectivity Booster in the Arc-Discharge Synthesis of Endohedral Fullerenes: Selective Synthesis of the Single-Molecule Magnet $Dy_2TiC@C_{80}$ and Its Congener $Dy_2TiC_2@C_{80}$



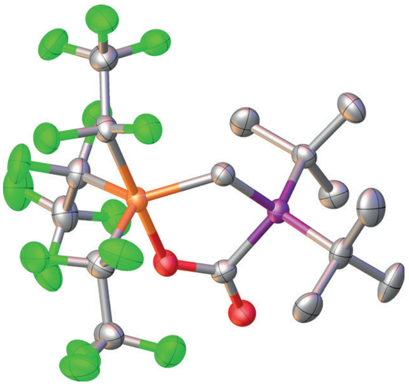
Carbide inclusion: The use of methane as a reactive gas dramatically increases the selectivity of the arc-discharge synthesis of $M_2TiC@C_{80}$ carbide clusterfullerenes (M = lanthanide). The new single-molecule magnet $Dy_2TiC@C_{80}$ could be readily isolated.

Frustrated Lewis Pairs

B. Waerder, M. Pieper, L. A. Körte,
T. A. Kinder, A. Mix, B. Neumann,
H.-G. Stammler,
N. W. Mitzel* ________ **13416 – 13419**

A Neutral Silicon/Phosphorus Frustrated Lewis Pair

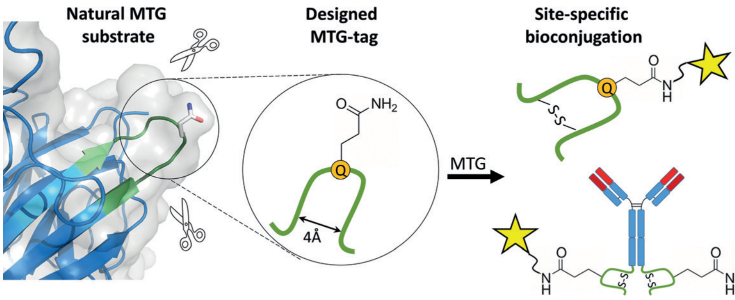
Yes, Si can! The first neutral frustrated Lewis pair system based on silicon, $(C_2F_5)_3SiCH_2P(tBu)_2$, was prepared from $(C_2F_5)_3SiCl$ and $LiCH_2P(tBu)_2$. This species binds CO_2 and SO_2 between its Lewis acidic and basic sites and cleaves dihydrogen (see structure with CO_2: C gray, F green, O red, P magenta, Si orange).



Bioconjugation

V. Siegmund, S. Schmelz, S. Dickgiesser,
J. Beck, A. Ebenig, H. Fittler,
H. Frauendorf, B. Piater, U. A. K. Betz,
O. Avrutina, A. Scrima, H.-L. Fuchsbauer,
H. Kolmar* 13420 – 13424

Locked by Design: A Conformationally Constrained Transglutaminase Tag Enables Efficient Site-Specific Conjugation



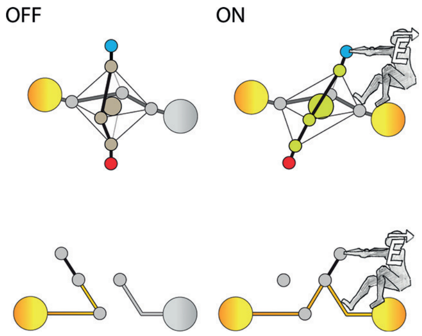
Really hits the spot: A novel tag for protein conjugation was engineered based on the crystal structure of a natural substrate for a bacterial transglutaminase. This conformationally locked structural mimic of the native conjugation site ensures site-selective and efficient protein ligation, as demonstrated for the therapeutic antibody cetuximab.

Molecular Electronics

G. D. Harzmann, R. Frisenda, H. S. J. van der Zant,* M. Mayor* 13425 – 13430

Single-Molecule Spin Switch Based on Voltage-Triggered Distortion of the Coordination Sphere

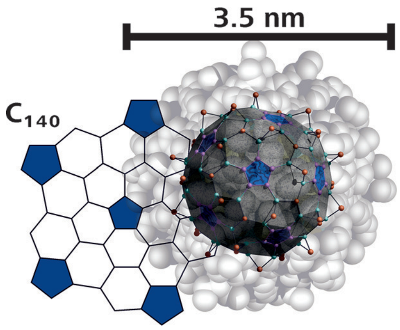
A “complex” switch: A novel single-molecule junction has been devised based on the coordination-sphere-dependent spin state of heteroleptic iron(II) terpyridine complexes.The perpendicular arrangement of two terpyridine (tpy) ligands in the complexe is distorted by the applied electric field. In the picture “Mr. *E*-Field” triggers a spin-crossover switch in a single-molecule junction.



Nanoclusters

S. Heinl, E. Peresypkina, J. Sutter,
M. Scheer* 13431 – 13435

Giant Spherical Cluster with *I*-C_{140} Fullerene Topology

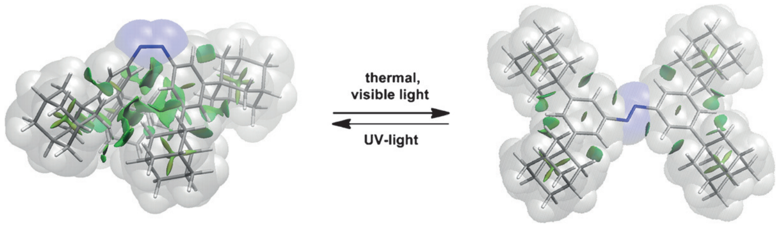


Change made it possible: The change from Cp* to the sterically highly demanding ligand Cp^{BIG} in the pentaphosphaferrocenes resulted in an effective expansion of the aggregate giant spherical cluster which has a diameter of about 3.5 nm. It exhibits structural analogy to the hitherto unknown *I*-C_{140} fullerene, a structural motif that has not yet been observed experimentally.

Noncovalent Interactions

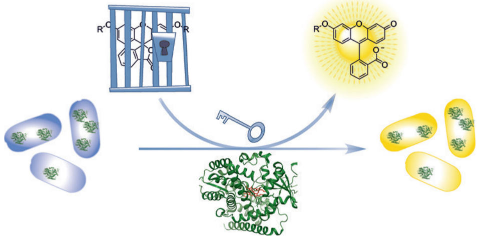
L. Schweighauser, M. A. Strauss,
S. Bellotto,
H. A. Wegner* 13436 – 13439

Attraction or Repulsion? London Dispersion Forces Control Azobenzene Switches



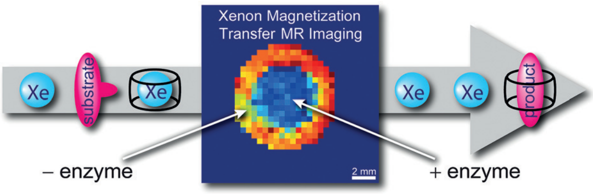
London’s calling: It is generally accepted that large alkyl substituents destabilize the *Z* isomer of double bonds. In the case of *meta*-substituted azobenzenes, it could be shown that the stability of the *Z* isomer increases as the size of the substituent grows. Computations show that the enhancement in stability is based on intramolecular London dispersion forces, which compete with steric hindrance in the *Z* isomers.

Protein Engineering



The great escape: Engineered cytochrome P450 monooxygenases were used for the removal of propargylic and benzylic ether protecting groups in vitro and in living *E. coli*. Deprotection resulted in the release of uncaged alcohols, which in this case display fluorescence properties. Such bioorthogonal enzyme/protecting group pairs could provide a means for the selective release of imaging agents or the catalytic activation of prodrugs at their site of action.

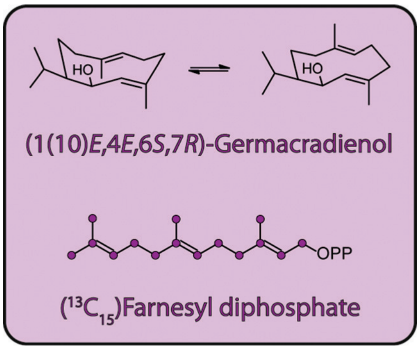
Xenon MRI



The supramolecular recognition properties of cucurbiturils are exploited in a modified signal-transfer approach in Xe NMR spectroscopy. Magnetic resonance imaging of enzymatic reactions was possible in this way by displacement of hyperpolarized ^{129}Xe.

Bacterial Terpenes

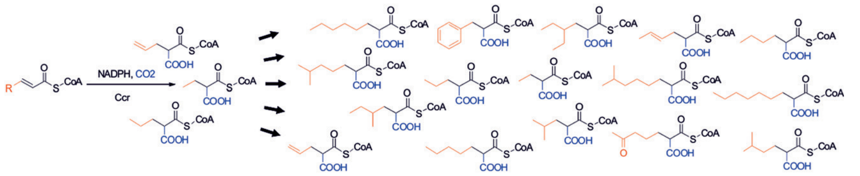
All 15 isotopomers of ($^{13}C_1$)- and fully labeled ($^{13}C_{15}$)farnesyl diphosphate were synthesized and converted to the title compound by a newly characterized bacterial terpene cyclase from *Streptomyces pratensis*. The enzyme products were used for structure elucidation of the sesquiterpene alcohol, full assignment of NMR data and a conformational analysis, and investigation of its Cope rearrangement and of its EI-MS fragmentation mechanism.



Nuclear Forensics

En route to nuclear reactors: When the first self-sustained nuclear chain reaction was initiated in 1942, projects focusing on the technical application of nuclear fission had also been launched in Germany. Two historic samples of uranium have now been studied in order to determine the source and age of the material and whether it had been exposed to any major neutron fluences.

Front Cover



CO_2 Fixation

D. M. Peter, L. Schada von Borzyskowski, P. Kiefer, P. Christen, J. A. Vorholt, T. J. Erb* ———— **13457 – 13461**

Screening and Engineering the Synthetic Potential of Carboxylating Reductases from Central Metabolism and Polyketide Biosynthesis

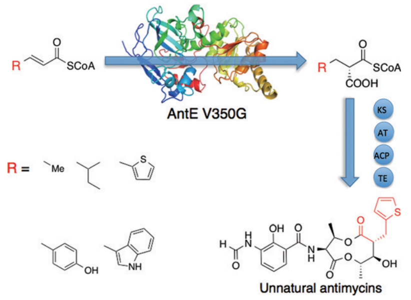
Engineering promiscuity: The molecular basis for substrate specificity of carboxylating enoyl-CoA reductases was identified by screening a CoA-thioester substrate library against a library of enzyme homologues. Site-directed mutagenesis of the promiscuity-determining sites enabled a previously restrictive enzyme to accept a variety of new, bulky substrates.

Polyketide Engineering

L. Zhang, T. Mori, Q. Zheng, T. Awakawa, Y. Yan, W. Liu, I. Abe* —— **13462 – 13465**

Rational Control of Polyketide Extender Units by Structure-Based Engineering of a Crotonyl-CoA Carboxylase/Reductase in Antimycin Biosynthesis

Extender unit engineering: The crotonyl-CoA carboxylase/reductase AntE was engineered to catalyze the carboxylation of a variety of substrates. By introducing the engineered AntE into a host strain, unnatural antimycins bearing a heterocyclic or substituted arene extender unit were biosynthesized.



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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