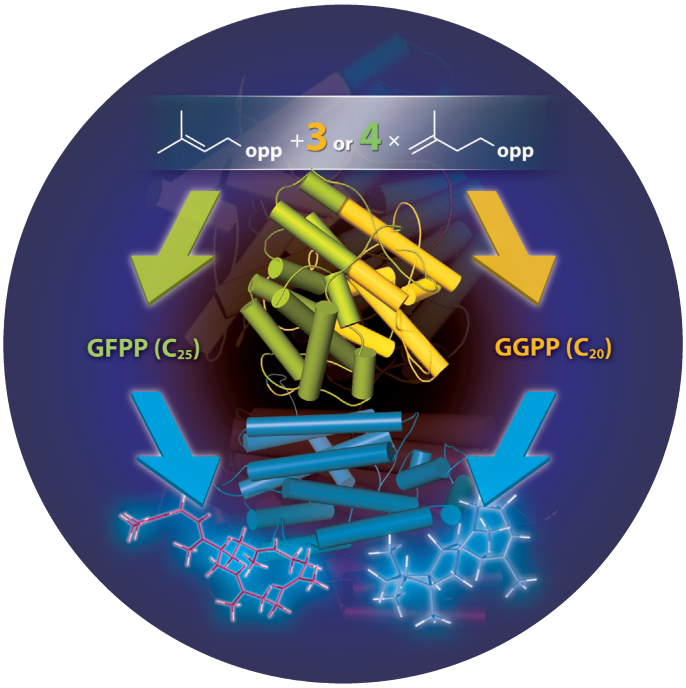
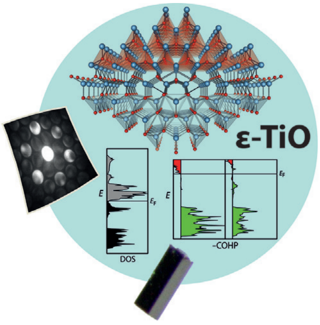
An unusual chimeric terpene synthase ...

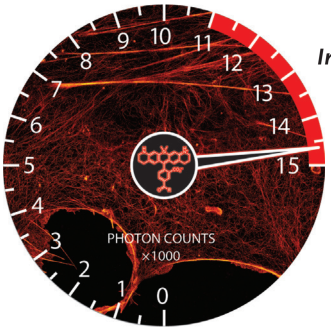


… (EvVS) was identified from *Emericella variecolor*. In their Communication on page 1658 ff., I. Abe and co-workers show that EvVS catalyzes both condensation and cyclization through its prenyltransferase (PT; green/yellow) and terpene cyclase (TC; turquoise) domains, respectively. Expression in *Aspergillus oryzae* led to a novel C_{20} diterpene, and domain swapping of the PT domain with that of a chimeric sesterterpene synthase led to a novel C_{25} sesterterpene.

Polymorphism

The synthesis of single crystals of a novel and stable TiO polymorph, ε-TiO, which is isotypic with ε-TaN, by using bismuth flux is described by R. Dronskowski, H. Yamane, and co-workers in their Communication on page 1652 ff.



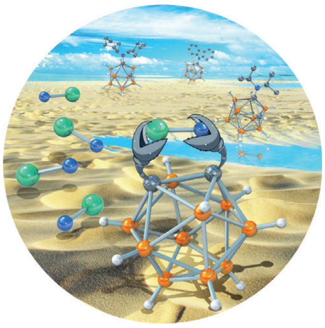


Imaging

Caged Si-Q-rhodamine is a red-shifted emitting label for localization microscopy. As L. D. Lavis and co-workers describe in their Communication on page 1723 ff., its emission is red-shifted enough to allow multicolor imaging.

Carboryne Amination

Preparing *N*-carboranyl amines is a challenging task. In their Communication on page 1751 ff., Z. Qiu, Z. Xie et al. describe a carboryne precursor that reacts with lithium amides to give a variety of *N*-carboranyl amines.



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Service

Author Profile

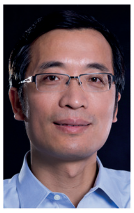
“In a spare hour, I enjoy a good glass of red wine and Bill Evans.
My biggest inspiration is my family …”
This and more about Andreas Marx can be found on page 1594.

News

R. J. Thomson

N. K. Garg

T. P. Yoon



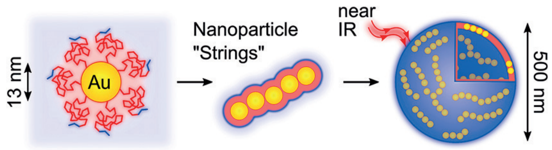
J. Hu

D. Rognan

M. J. Gaunt

Highlights

Nanoparticle Assemblies



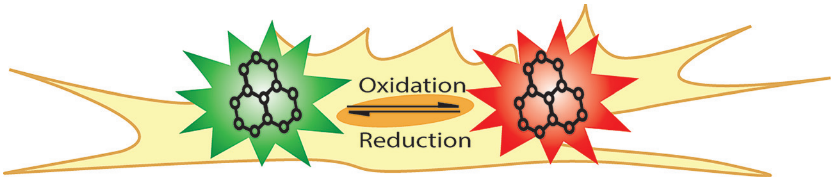
Function at all scales: Hierarchical assemblies of nanoparticles provide routes to multifunctional materials, in which structures at different scales impart different functions. Plasmonic vesicles formed by nanoparticle “strings” are useful both as contrast agents for photoacoustic imaging and as light-activated drug-delivery vehicles.

Minireviews

Biosensors

A. Kaur, J. L. Kolanowski,
E. J. New* ______ 1602 – 1613

Reversible Fluorescent Probes for Biological Redox States



A good image: Chemical tools to study redox biology are crucial in understanding physiological and pathological processes. It is particularly important to be able to reversibly sense changes in redox state over time. The current progress towards such probes is described in this review, as well as identification of key directions for future research in this nascent field of vital biological interest.

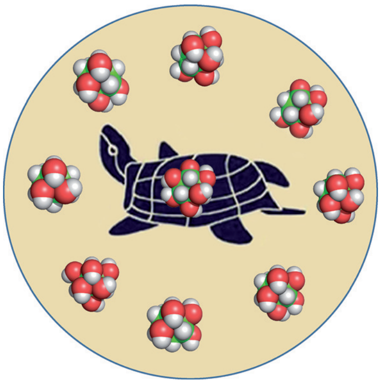
Reviews

Inositols

M. P. Thomas, S. J. Mills,
B. V. L. Potter* ______ 1614 – 1650

The “Other” Inositols and Their Phosphates: Synthesis, Biology, and Medicine (with Recent Advances in *myo*-Inositol Chemistry)

Turtle reconfiguration: “Agranoff’s Turtle”, used to visualize *myo*-inositol, with head, tail, and limbs rearranged yields another eight stereoisomers. These have different properties in biological systems, and some may have medical applications. All can be synthesized by a variety of routes, but are much less studied than *myo*-inositol. The synthesis and roles of these isomers and their phosphates are discussed, with recent advances in *myo*-inositol chemistry.



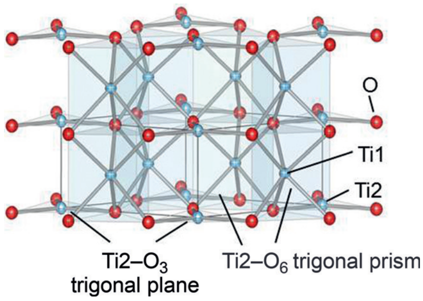
Communications

Polymorphism

S. Amano, D. Bogdanovski, H. Yamane,*
M. Terauchi,
R. Dronskowski* ______ 1652 – 1657

ε-TiO, a Novel Stable Polymorph of Titanium Monoxide

A new TiO polymorph: Single crystals of a novel TiO polymorph, ε-TiO, which is isotypic with ε-TaN, were synthesized by using a bismuth flux. First-principles calculations show that ε-TiO is more stable than the known low-temperature phase α-TiO, which has a defective rock-salt-type structure.



Frontispiece

For the USA and Canada:
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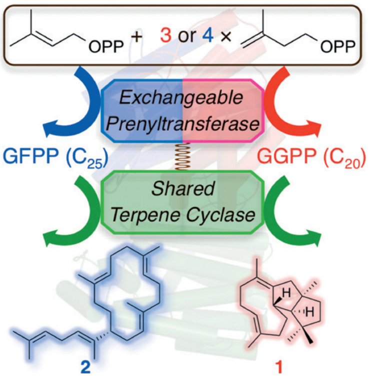
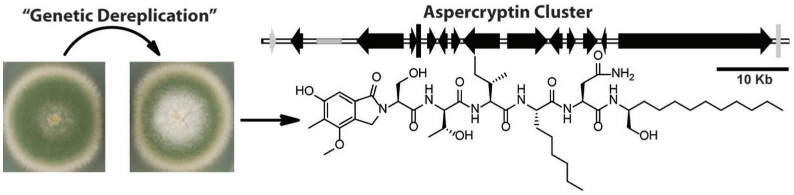
Biosynthesis

Front Cover

Swap and share: The unusual chimeric terpene synthase EvVS, which catalyzes both condensation and cyclization reactions, was identified from *Emericella variecolor*. EvVS produces both the novel C_{20} diterpene variediene (**1**) and a C_{25} sesterterpene (**2**) in vitro. Rational domain swapping of the PT domain of EvVS with that of another chimeric sesterterpene synthase successfully led to efficient in vivo production of **2**.

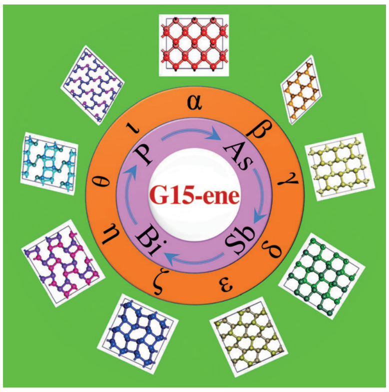


Natural Products



Cutting through the mix: Deletion of eight of the most highly expressed secondary metabolite gene clusters in *Aspergillus nidulans* enabled the isolation of a new natural product, aspercryptin. This unusual product is biosynthesized by the combination of one known and one unexplored biosynthetic pathway.

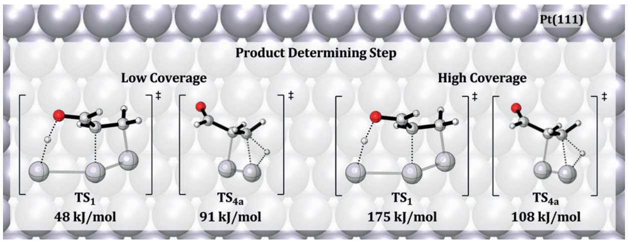
Group 15 Monolayers



The attractive broad range of band gaps and high mobilities of a 2D semiconductor family, namely phosphorene, arsenene, antimonene, and bismuthene, is presented. These Group 15 monolayers have significantly varied energy band gaps, which are crucial for broadband photoresponse. More importantly, puckered phosphorene, arsenene, and buckled bismuthene possess carrier mobilities as high as several thousand $cm^2 V^{-1} s^{-1}$.

Surface Chemistry

VIP

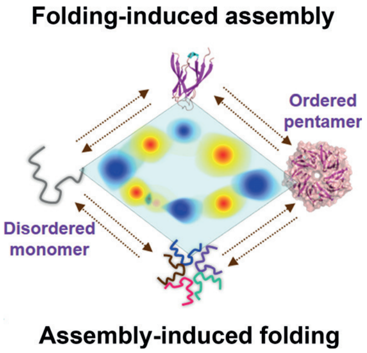


Run for cover: Acrolein is reduced chemoselectively on Pt(111) and Pd(111) surfaces at the C=C bond and not at the C=O bond because reaction steps involving C=O reduction become energetically unfavorable with increasing steric repulsion.

Protein Folding and Assembly

P. R. Banerjee, D. M. Mitrea,
R. W. Kriwacki,*
A. A. Deniz* ______ 1675 – 1679

Asymmetric Modulation of Protein Order–Disorder Transitions by Phosphorylation and Partner Binding

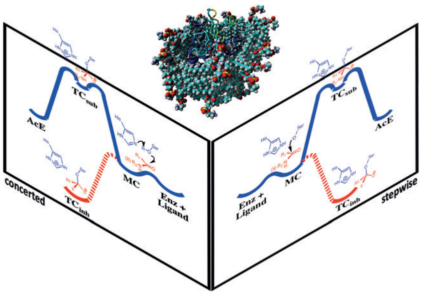


A plastic landscape was found to facilitate the functional shape shifting of an oncogenic protein. Alternative folding–assembly pathways of this conditionally disordered protein (see picture) were revealed by single-molecule and ensemble experiments. Posttranslational modification and partner binding had differential effects on individual steps and were able to counteract each other.

Enzyme Catalysis

N. Uritsky, M. Shokhen,*
A. Albeck* ______ 1680 – 1684

Stepwise Versus Concerted Mechanisms in General-Base Catalysis by Serine Proteases



It comes down to more or less water: How do proteases perform general-base catalysis? A computational study suggests different mechanisms for water-soluble chymotrypsin and membrane-embedded rhomboid. The concerted and stepwise mechanisms differ because of the dynamically changing pK_a values of the catalytic residues as a function of their progressively reduced water exposure, which is caused by the incoming ligand.

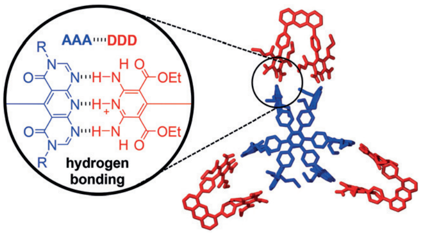
Hydrogen Bonds

M. Papmeyer, C. A. Vuilleumier,
G. M. Pavan, K. O. Zhurov,
K. Severin* ______ 1685 – 1689

Molecularly Defined Nanostructures Based on a Novel AAA–DDD Triple Hydrogen-Bonding Motif

Inside Cover

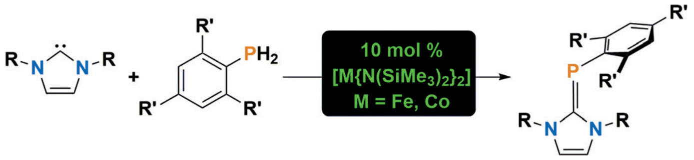
Made to connect: A new synthetic method provides facile access to supramolecular building blocks with multiple AAA or DDD groups (A = acceptor, D = donor). The components assemble by forming stable AAA–DDD triple hydrogen bonds to give macrocycles or a macrobicyclic complex (see scheme).



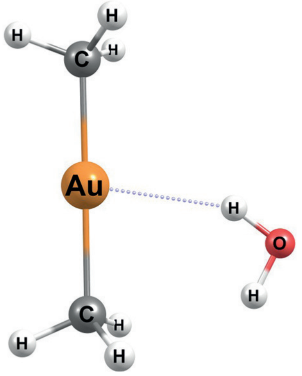
Carbenes

K. Pal, O. B. Hemming, B. M. Day,
T. Pugh, D. J. Evans,
R. A. Layfield* ______ 1690 – 1693

Iron- and Cobalt-Catalyzed Synthesis of Carbene Phosphinidenes



Carbene phosphinidenes of the type (NHC)·PAr (NHC = N-heterocyclic carbene) can be synthesized using a catalytic phosphinidene-transfer reaction between primary phosphines and NHCs, with the simple iron or cobalt amide, $[M\{N(SiMe_3)_2\}_2]$ (M = Fe or Co), as the catalyst.



A computational study has conclusively shown that Au^I can act as a hydrogen-bond acceptor towards water molecules. The overall interaction can be supported by co-operative, synergistic hydrogen bonding, particularly when the coordinated ligands contain hydrogen-bond donors.

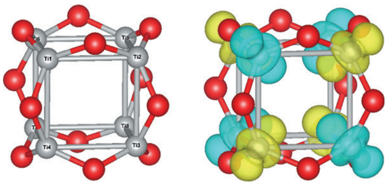
Hydrogen Bonding

F. Groenewald, J. Dillen,
H. G. Raubenheimer,
C. Esterhuysen* ________ **1694 – 1698**

Preparing Gold(I) for Interactions with Proton Donors: The Elusive [Au]···HO Hydrogen Bond

---

A high-symmetry geometric structure of the bare Ti_8O_{12} cluster was calculated and found to be in excellent agreement with experimental results. The origin of the stability is a unique chemical bonding where eight electrons of Ti atoms interact with each other in antiferromagnetic fashion to lower the total energy of the system. The bare Ti_8O_{12} is thus an unusual molecule stabilized by d-orbital antiferromagnetic coupling.

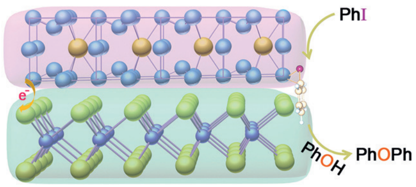


Titanium Clusters

X. Yu,* A. R. Oganov, I. A. Popov, G. Qian,
A. I. Boldyrev ________ **1699 – 1703**

Antiferromagnetic Stabilization in the Ti_8O_{12} Cluster

The electrophilicity and nucleophilicity in two-dimensional heteronanostructures can be tuned by interface engineering, which triggers the transfer of electrons across the interface. For example, the Cu_2S/MoS_2 heteronanostructure thus obtained is a superior catalyst for Ullmann couplings with excellent stability and recyclability.

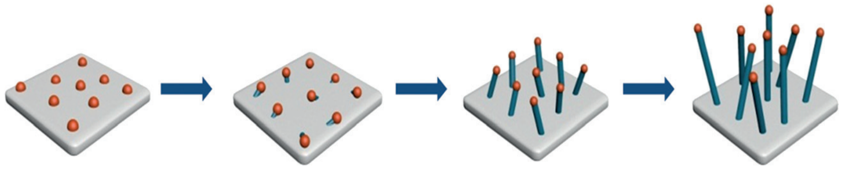


Heterogeneous Catalysis

X. Sun, H. T. Deng, W. G. Zhu, Z. Yu,
C. Z. Wu,* Y. Xie ________ **1704 – 1709**

Interface Engineering in Two-Dimensional Heterostructures: Towards an Advanced Catalyst for Ullmann Couplings

---



Crystal engineering: Solution-liquid-solid (SLS) synthesis has been brought into the realm of conventional low-temperature solution synthesis through the use of a nonmetal molecular crystal as a catalyst. This approach has been demonstrated by using selenium as the catalyst for the synthesis of hexagonal nickel selenide nanowire arrays, which were used for electrochemical water oxidation.

Nanowires

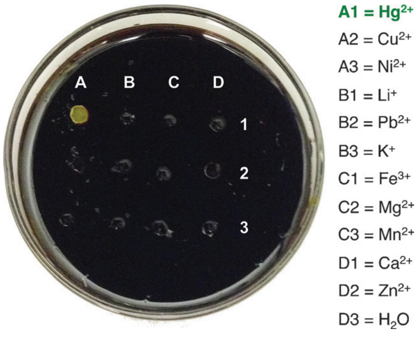
K. Xu, H. Ding, K. C. Jia, X. L. Lu,
P. Z. Chen, T. P. Zhou, H. Cheng, S. Liu,
C. Z. Wu,* Y. Xie ________ **1710 – 1713**

Solution-Liquid-Solid Synthesis of Hexagonal Nickel Selenide Nanowire Arrays with a Nonmetal Catalyst

Sustainable Materials

M. P. Crockett, A. M. Evans,
M. J. H. Worthington, I. S. Albuquerque,
A. D. Slattery, C. T. Gibson, J. A. Campbell,
D. A. Lewis, G. J. L. Bernardes,
J. M. Chalker* ______ 1714 – 1718

Sulfur-Limonene Polysulfide: A Material Synthesized Entirely from Industrial By-Products and Its Use in Removing Toxic Metals from Water and Soil



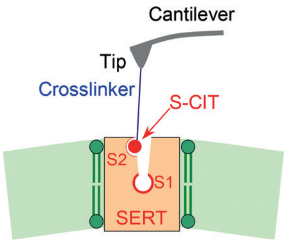
Waste not: A polysulfide has been synthesized from the industrial by-products sulfur and limonene. The material can be processed into coatings or molded into objects and responds selectively to mercury(II), producing a bright yellow deposit that adheres to the material (see picture). The use of the polysulfide in water and soil remediation is demonstrated.

Nanopharmacology

R. Zhu, D. Sinwel, P. S. Hasenhuetl,
K. Saha, V. Kumar, P. Zhang, C. Rankl,
M. Holy, S. Sucic, O. Kudlacek, A. Karner,
W. Sandtner, T. Stockner, H. J. Gruber,
M. Freissmuth, A. Hauck Newman,
H. H. Sitte, P. Hinterdorfer* 1719 – 1722

Nanopharmacological Force Sensing to Reveal Allosteric Coupling in Transporter Binding Sites

Methods for direct measurement of the interaction forces between the serotonin transporter and the *S*- and *R*-enantiomers of citalopram (CIT) on the single-molecule level allows the demonstration of two distinct populations of characteristic binding strengths, which provide physical evidence for the existence of two binding sites *S1* and *S2* that are allosterically coupled and exert reciprocal modulation. SERT = serotonin transporter.



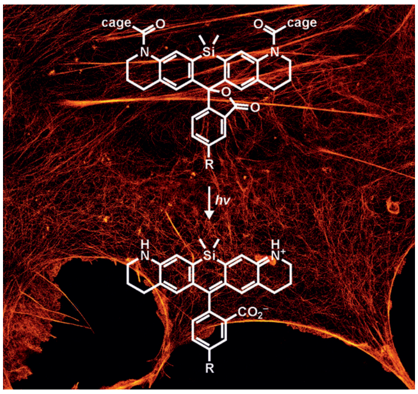
Multicolor Imaging

J. B. Grimm, T. Klein, B. G. Kopek,
G. Shtengel, H. F. Hess, M. Sauer,
L. D. Lavis* ______ 1723 – 1727

Synthesis of a Far-Red Photoactivatable Silicon-Containing Rhodamine for Super-Resolution Microscopy

Inside Back Cover

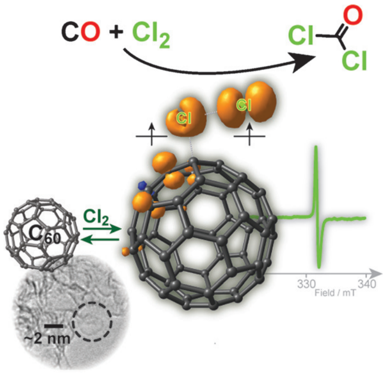
In the red zone: Caged Si-Q-rhodamine, a new red-shifted label for localization microscopy, exhibits superior photon counts and is sufficiently red-shifted to allow multicolor imaging. This dye is a useful label for advanced imaging experiments and constitutes a new scaffold for red fluorogenic molecules.



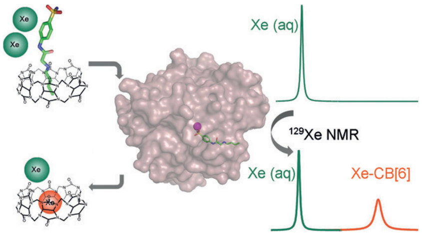
Radical Reactions

N. K. Gupta, A. Pashigreva, E. A. Pidko,*
E. J. M. Hensen, L. Mleczko, S. Roggan,*
E. E. Ember,* J. A. Lercher* 1728 – 1732

Bent Carbon Surface Moieties as Active Sites on Carbon Catalysts for Phosgene Synthesis



Active sites and reactive intermediates: Experiments and DFT calculations provide insight into the mechanism of carbon-catalyzed Cl_2 activation and $COCl_2$ formation. The structural resemblance between the C_{60} fullerene and active carbon catalysts showed that carbon sites distorted from sp^2 coordination in nonplanar units are the active sites, catalyzing the process via an active $[C_{60}\cdots Cl_2]$ complex.

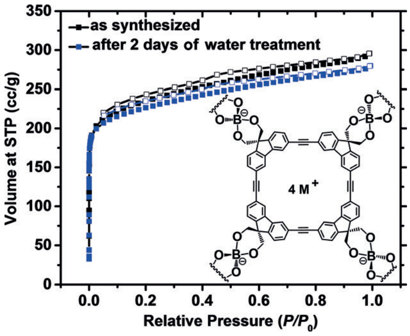


Be my guest: A cucurbit[6]uril (CB[6])-based molecular relay enables detection of proteins by using ^{129}Xe NMR. A two-faced guest (TFG) initially binds CB[6]. Upon addition of the cognate target, the TFG is sequestered by the protein target, thereby freeing CB[6] and allowing it to bind to xenon. The TFG is engineered such that the CB[6]–^{129}Xe NMR signal is absent until the addition of the target protein.

Biosensors

Y. Wang, B. W. Roose, J. P. Philbin, J. L. Doman, I. J. Dmochowski* ________ **1733 – 1736**

Programming A Molecular Relay for Ultrasensitive Biodetection through ^{129}Xe NMR



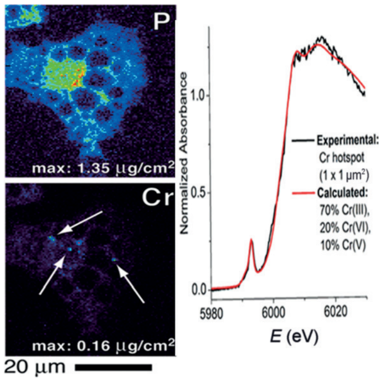
Covalent organic frameworks linked by ionic spiroborates were prepared, which exhibit excellent gas uptake properties, resistance to hydrolysis, and room-temperature ion conductivity. The highly stable COFs can potentially serve as absorbents for alternative energy sources such as hydrogen or methane and also as solid lithium electrolytes for the next-generation lithium batteries.

Microporous Materials

Y. Du, H. Yang, J. M. Whiteley, S. Wan, Y. Jin, S. Lee,* W. Zhang* ____ **1737 – 1741**

Ionic Covalent Organic Frameworks with Spiroborate Linkage

Dangerous oxidation: Synchrotron-based single-cell mapping and XANES spectroscopic techniques revealed the formation of chromium hotspots containing mixtures of Cr^{III}, Cr^{V}, and Cr^{V} species in cultured mouse adipocytes that had been treated with Cr^{III} dietary supplements. These findings provide evidence for the hypothesis that the consumption of such supplements may pose a cancer risk.



Bioinorganic Chemistry

L. E. Wu, A. Levina, H. H. Harris, Z. Cai, B. Lai, S. Vogt, D. E. James, P. A. Lay* ________ **1742 – 1745**

Carcinogenic Chromium(VI) Compounds Formed by Intracellular Oxidation of Chromium(III) Dietary Supplements by Adipocytes

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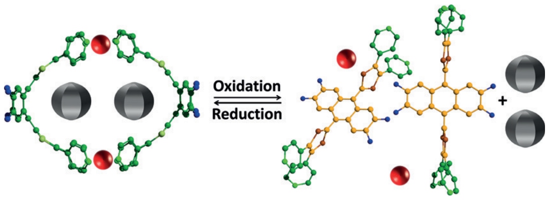


Redox-controlled guest binding: A redox-active coordination cage based on the extended tetrathiafulvalene framework could be disassembled upon oxidation and reassembled upon reduction through drastic conformational changes. This reversible process makes it possible to control the binding and release of an anionic guest.

Supramolecular Chemistry

V. Croué, S. Goeb,* G. Szalóki, M. Allain, M. Sallé* ________ **1746 – 1750**

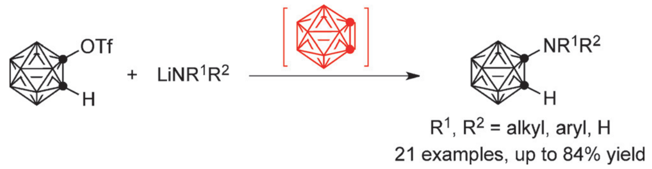
Reversible Guest Uptake/Release by Redox-Controlled Assembly/Disassembly of a Coordination Cage

Carboryne Amination

R. Cheng, J. Zhang, J. Zhang, Z. Qiu,*
Z. Xie* ______ 1751 – 1754

Facile Synthesis of *N*-Carboranyl Amines through an *ortho*-Carboryne Intermediate

Back Cover

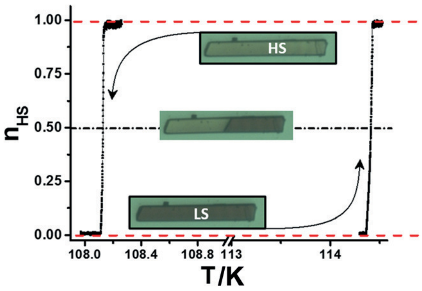


An efficient *o*-carboryne precursor 1-Li-2-OTf-*o*-$C_2B_{10}H_{10}$ has been developed, which undergoes addition with lithium amides to give a series of *N*-carboranyl amines in moderate to high yields with a broad substrate scope. This represents the first general method for the synthesis of 1-R^1R^2N-*o*-carboranes.

Spin Crossover

M. Sy, D. Garrot, A. Slimani,
M. Páez-Espejo, F. Varret,
K. Boukheddaden* ______ 1755 – 1759

Reversible Control by Light of the High-Spin Low-Spin Elastic Interface inside the Bistable Region of a Robust Spin-Transition Single Crystal

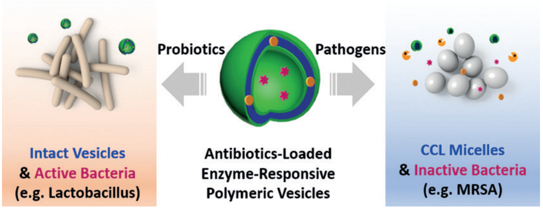


Spin cycle: Illuminating one end of a spin-crossover single crystal with a low intensity laser could reversibly change the spin state from low spin (LS) to high spin (HS). The progress of the transition along the crystal could be observed by light microscopy. The crystal maintained its integrity over several cycles suggesting applications in actuation, micro-positioning, and switching devices.

Polymeric Vesicles

Y. Li, G. Liu, X. Wang, J. Hu,
S. Liu* ______ 1760 – 1764

Enzyme-Responsive Polymeric Vesicles for Bacterial-Strain-Selective Delivery of Antimicrobial Agents

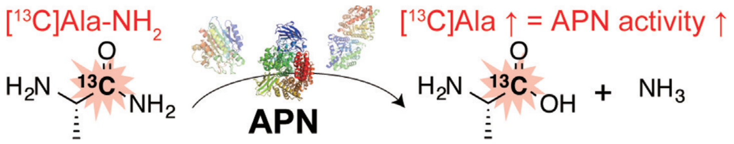


Smart delivery: Stimuli-responsive polymeric vesicles deliver antibiotics in response to specific enzymes including penicillin G amidase (*PGA*) and β-lactamase (*Bla*), which are relevant to drug-resistant bacterial strains. Antibiotic-loaded vesicles undergo self-immolative structural rearrangement and morphological transitions, leading to sustained antibiotic release.

Biosensors

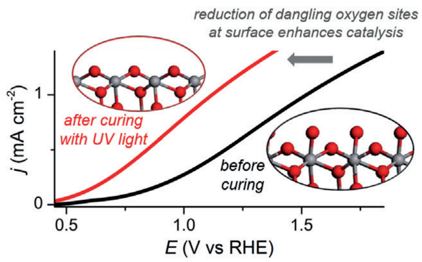
R. Hata, H. Nonaka, Y. Takakusagi,
K. Ichikawa, S. Sando* ______ 1765 – 1768

Design of a Hyperpolarized Molecular Probe for Detection of Aminopeptidase N Activity

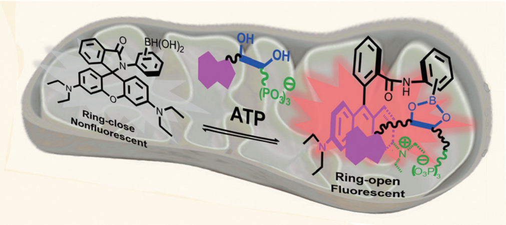


Rational design: A hyperpolarized NMR probe [1-^{13}C]Ala-NH_2 was designed. The probe satisfies the prerequisites for aminopeptidase N (APN) detection, namely, sufficient retention of the hyperpolarized state, high reactivity towards APN, and an APN-induced chemical shift change. The probe allowed sensitive detection of APN activity using ^{13}C NMR spectroscopy.

UV curing enhances activity: Exposure of $BiVO_4$ photoanodes to ultraviolet radiation yields a cathodic shift in onset potential and an improvement in photocurrent of water oxidation comparable to the effects of electrocatalysts.

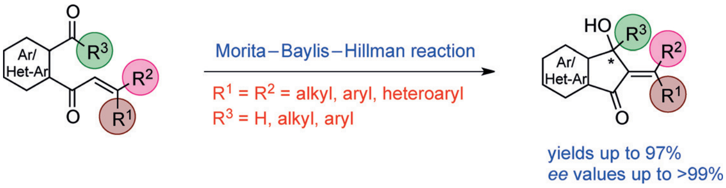


Photoelectrocatalysis



Illuminating the ATP: A multisite-binding, switchable fluorescent probe can selectively and rapidly respond to ATP at intracellular concentrations. In live-cell imaging, the probe was successfully applied to monitor fluctuations in mitochondrial ATP levels.

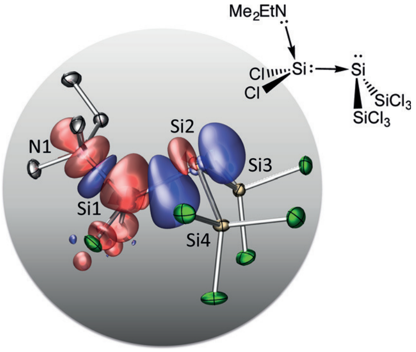
Fluorescent Probes



A solution after 47 years: The first enantioselective organophosphine-catalyzed intramolecular Morita–Baylis–Hillman (MBH) reaction of sterically and electronically highly demanding β-mono- and β,β-disubstituted enones is reported. This strategy provides access to cyclopenta[*b*]annulated arenes and heteroarenes in excellent enantiopurities and near-quantitative yields in remarkably short reaction times.

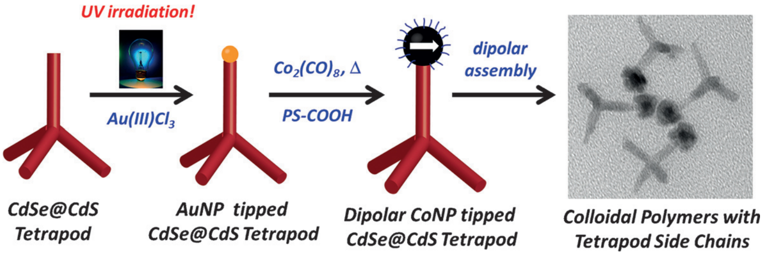
Organocatalysis

Give and take: A perchlorodisilene amine adduct with an unusually bent structure (see picture) was isolated by freeze-quench crystallization. The quantum-chemical bond analysis discloses dative N1→Si1 and Si1→Si2 bonds leading to a push–pull stabilization of the central $SiCl_2$ group.



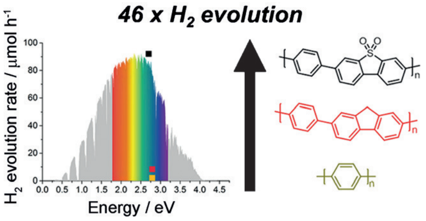
Silicon Chemistry

Nanoparticle Assembly



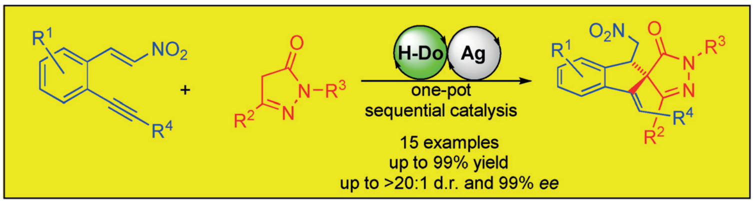
Mimicking *t*Bu: A heterostructured semiconductor CdSe@CdS tetrapod that carries a single Co nanoparticle tip was synthesized. The key step in the synthesis was the selective deposition of a single AuNP tip onto the CdSe@CdS tetrapod under UV-irradiation. Colloidal polymers that carry the semiconductor tetrapod as a side chain group attached to the CoNP colloidal polymer main chain were prepared.

Photocatalysis



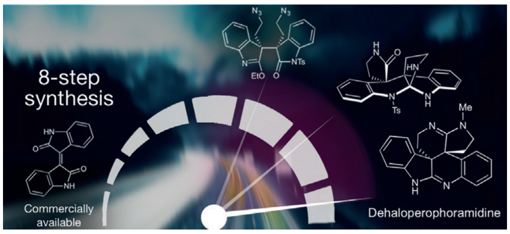
Boosting H$_2$ production: Introduction of planarized fluorene, carbazole, dibenzo[*b*,*d*]thiophene, or dibenzo[*b*,*d*]thiophene sulfone units in linear poly(*p*-phenylene)s greatly enhances the H$_2$ evolution rate. The most active dibenzo[*b*,*d*]thiophene sulfone co-polymer has a UV photocatalytic activity that rivals TiO$_2$, but is much more active under visible light.

Asymmetric Synthesis

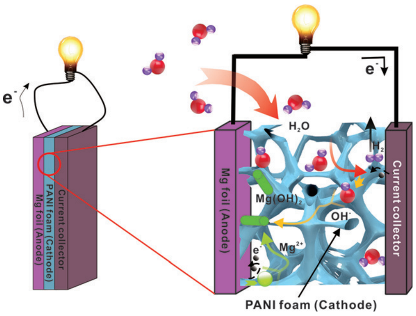


Silver lining: A stereoselective one-pot synthesis of spiropyrazolones through an organocatalytic asymmetric Michael addition and a formal Conia-ene reaction has been developed. Silver catalysis plays a pivotal role for the cyclization, however metal-free alternatives have been found in some cases. The mechanism was investigated by quantum chemical computations. H-Do = hydrogen-bonding donor.

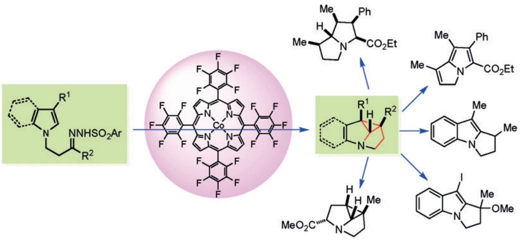
Natural Product Synthesis



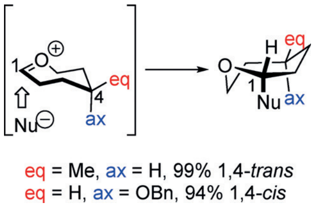
Fast and furious: The eight-step synthesis of dehaloperophoramidine, a polycyclic indole alkaloid, is achieved by incorporating two substrate-specific domino processes. The discovery of these processes resulted from a retrosynthetic analysis in which all skeletal atoms and all functional groups required to reach the target molecule were incorporated at an early stage of the sequence.



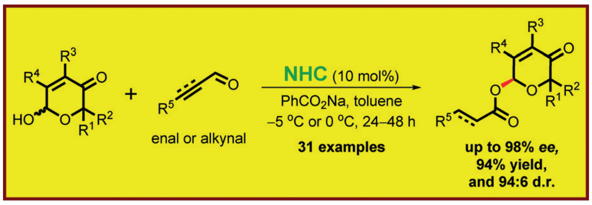
A shocking touch: A simple battery is developed by direct contact of magnesium foil with ultralight polyaniline (PANI) foam. Electrical current is steadily released from the junction with a specific energy of 646 $\mathrm{mWh\,g^{-1}}$ and specific capacity of 1247 $\mathrm{mAh\,g^{-1}}$. Additionally, the battery offers an environmentally friendly route to hydrogen production.



Not your common ring variety: The title reaction gives a range of nitrogen-containing polycyclic compounds in moderate to high yields. The thus obtained N-containing polycyclic compounds can be converted into a variety of N-heterocycles with potential synthetic and biological interest.

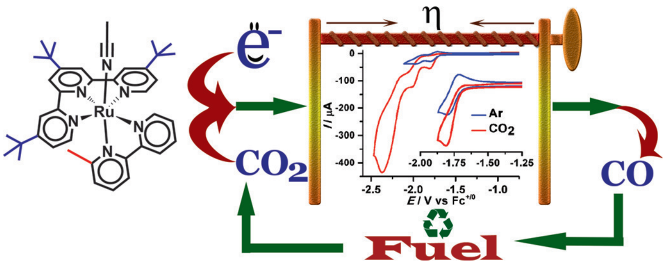


At sixes and sevens: Nucleophilic attack on seven-membered-ring oxocarbenium ions is generally highly stereoselective. The preferred mode of nucleophilic attack (see scheme) forms the product in a conformation that minimizes transannular interactions, thus leading to different stereoselectivity to that observed for reactions involving six-membered-ring oxocarbenium ions.



Sweet products: The dynamic kinetic resolution of 6-hydroxypyranones with enals or alkynals through an asymmetric redox esterification is catalyzed by a chiral N-heterocyclic carbene (NHC). The resulting esters are obtained in good to high yields and with high levels of enantio- and diastereocontrol.

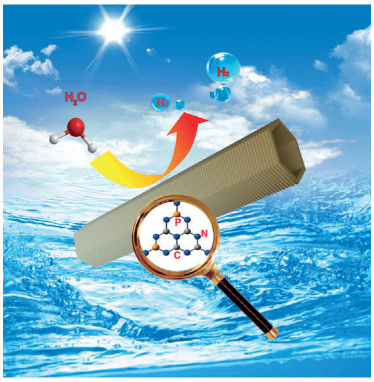
Electrocatalysis



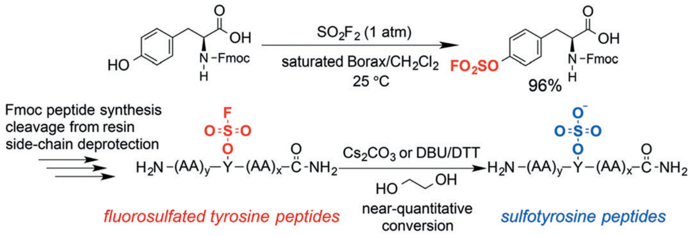
Simple and effective: The steric effect of a CH_3 group at the *ortho* position of a bipyridine ligand activates a previously unreactive oxidation state in a Ru^{II} polypyridyl complex and enables electrocatalytic CO_2 reduction at the potential of the first one-electron reduction. The mechanistic pathway operates at an overpotential of $\eta = 0.47$ V, about 400 mV less than in the absence of the methyl group.

Hydrogen Evolution Catalysts

Phosphorus-doped hexagonal carbon nitride tubes were obtained from a rod-like supramolecular precursor through phosphorous acid assisted hydrothermal and subsequent thermal treatment. It exhibits a high visible-light photocatalytic hydrogen evolution performance that is better than most reported bulk carbon nitrides, which is due to the hierarchical micro-nanostructure and P doping.

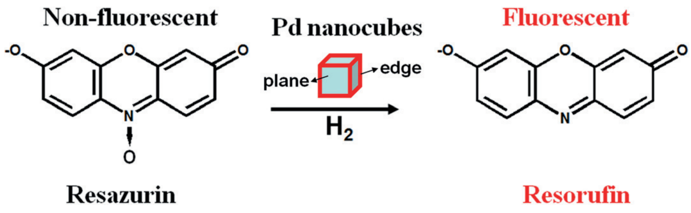


Peptide Synthesis



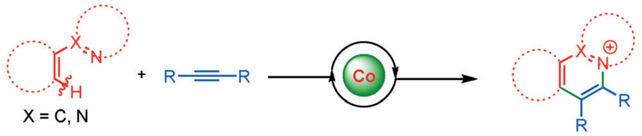
SuFEx for success: A facile Fmoc-based solid-phase synthesis of fluorosulfated tyrosine peptides is reported, enabled by a one-step synthesis of Fmoc-fluorosulfated tyrosine. An efficient ethylene glycolysis method for the transformation of side-chain-deprotected fluorosulfated tyrosine peptides into sulfotyrosine peptides is key for success.

Nanocatalysis



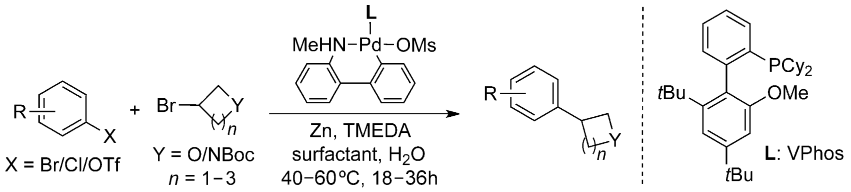
One at a time: The catalytic kinetics and dynamics of the different types of surface atoms (plane and edge) were revealed for the first time by a statistical quantitative deconvolution of observables obtained from traditional single-molecule nanocatalysis of Pd nanocrystals.

C–H Activation



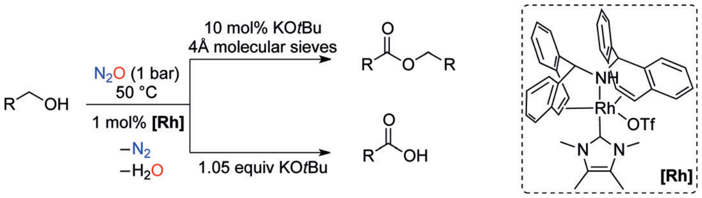
Salty rings: Four oxidative annulation reactions of arenes with alkynes proceeds through cobalt-catalyzed pyridine-, azo-, and imine- directed *ortho* C–H activation to synthesize various heterocyclic ammonium salts. The reactions tolerate a wide substrate scope and preliminary mechanistic studies are discussed.

Micellar Catalysis



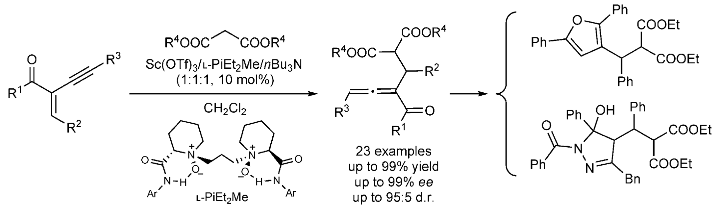
Happy to get its feet wet: VPhos was developed as a hybrid ligand incorporating structural elements of existing ligands for improved activity in the micelle-enhanced palladium-catalyzed cross-coupling of non-aromatic O- and N-heterocyclic alkyl bromides with (hetero)aryl halides (see scheme). The Pd/VPhos catalyst (5 mol%) and a simple surfactant system based on octanoic acid enabled the efficient synthesis of a broad range of alkylated (hetero)arenes.

Coupling Reactions



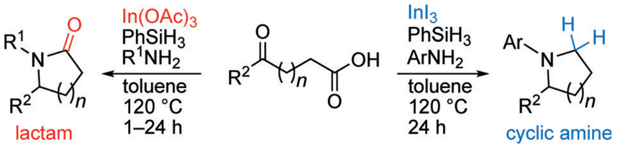
The use of N_2O as a hydrogen acceptor in the dehydrogenative coupling of primary alcohols leads to the formation of N_2 and H_2O as the only side products. This transformation, which is catalyzed by a bis(olefin)amine rhodium(I) complex under mild conditions, was shown to have a broad substrate scope.

Asymmetric Catalysis



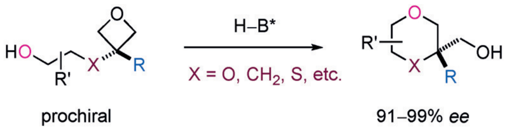
An *N*,*N*′-dioxide/Sc^{III} complex catalyzed conjugate addition of malonic esters to enynes is described. A range of trisubstituted 1,2-allenyl ketones were obtained in high yields with good d.r. and excellent *ee* values. Moreover, the products could be easily transformed to pharmacologically important chiral furan and 5-hydroxypyrazoline derivatives.

Cyclizations



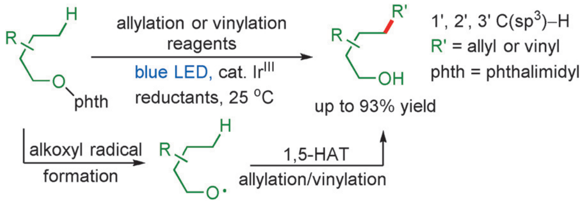
Making the switch: Catalytic construction of *N*-substituted lactams from keto acids and primary amines using an In(OAc)$_3$/PhSiH$_3$ reducing system was achieved. A variety of functional groups can be tolerated during the transformation. By simply changing the catalyst from In(OAc)$_3$ to InI$_3$, the cyclic amines, rather than lactams, are formed from the same starting materials.

Asymmetric Catalysis



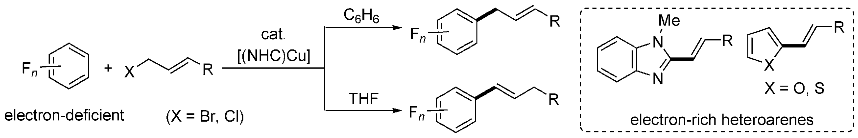
From ring to ring: A unified approach for the synthesis of chiral 1,4-dioxanes and other oxygen heterocycles is based on an organocatalytic enantioselective desymmetrization of oxetanes by alcohols. The reaction proceeds, even in the presence of multiple hydrogen-bonding sites, with exceedingly high efficiency.

Photochemistry



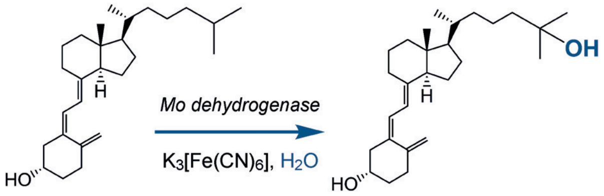
A HAT trick: A visible-light-induced formation of alkoxyl radicals from N-alkoxyphthalimides is reported, and the Hantzsch ester as the reductant is crucial in the reaction. The selective hydrogen-atom abstraction by the alkoxyl radical enables regio- and chemoselective C(sp^3)–H allylation and alkenylation reactions at room temperature. A broad substrate scope is tolerated. HAT = hydrogen-atom transfer.

Allylic Compounds



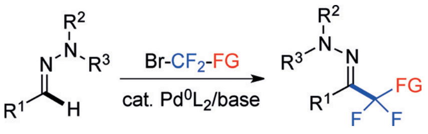
Something new for Cu: New reactivity of a [Cu(NHC)] (NHC = N-heterocyclic carbene) catalyst is disclosed for the direct C–H allylation and alkenylation of both electron-deficient polyfluoroarenes and electron-rich heteroarenes. This catalyst system leads to mild reaction conditions, broad scope with respect to the arenes and allyl halides, good functional-group tolerance, and high stereoselectivity.

Biocatalysis



Well PrepareD: Oxygen-independent, regioselective, and complete hydroxylation of the tertiary C25 of vitamin D_3 to its circulating 25-hydroxy form was catalyzed by a Mo-containing dehydrogenase from a denitrifying bacterium grown with cholesterol. This electron-donor-independent system can be used for the enzymatic synthesis of the clinically most relevant form of vitamin D.

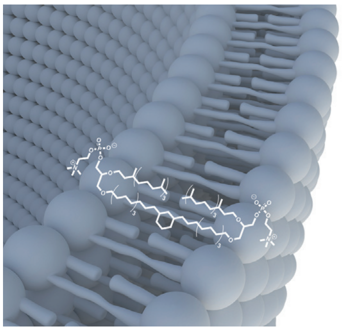
Homogeneous Catalysis



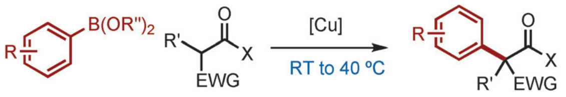
Single file: The title reaction was established as a new and versatile synthetic entry to α,α-difluoro carbonyl compounds. On the basis of preliminary studies, the proposed mechanism involves a radical/single-electron transfer process via a difluoroalkyl radical intermediate.

Synthetic Lipids

Extremophile Archaeal organisms thrive in harsh environments in part as a result of the unusual structural features present in their lipids. A systematic study of synthetic lipids reveals that membrane tethering and incorporation of cyclohexane rings into the tethered segment are two key structural features present in natural archaeal lipids that can improve membrane integrity by decreasing membrane permeability to small ions.



Synthetic Methods



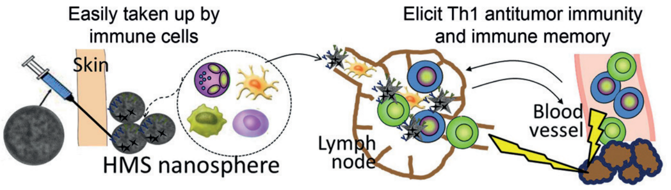
- mild reaction conditions
- complements cross-coupling/S_NAr
- tolerates aryl/alkyl halides
- enolate can be secondary or tertiary

Putting it mildly: Under mild reaction conditions, $Cu(OTf)_2$ mediates the coupling of functionalized aryl boron species with a variety of stabilized sp^3-nucleophiles. Tertiary malonates and 1,3-amido esters can be employed as substrates to generate quaternary centers. The transformation is chemoselective in the presence of halogen electrophiles, including aryl bromides and iodides. EWG = electron-withdrawing group.

Cancer Therapy

X. Wang,* X. Li, A. Ito, Y. Watanabe,
Y. Sogo, N. M. Tsuji,
T. Ohno ________ 1899 – 1903

Stimulation of In Vivo Antitumor Immunity with Hollow Mesoporous Silica Nanospheres

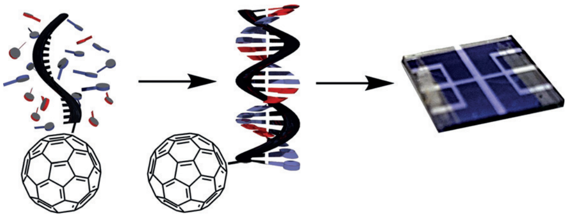


Appropriate adjuvants that support the generation of a robust and long-lasting antitumor immune response are crucial for tumor immunotherapy. Hollow mesoporous silica (HMS) nanospheres markedly improve the antitumor immunity, the Th1 and Th2 immunity, and the $CD4^+$ and $CD8^+$ effector memory T cell population in bone marrow in vivo and may thus be used as immunoadjuvants to treat cancer in humans.

Organic Photovoltaics

P. Ensslen, S. Gärtner, K. Glaser,
A. Colsmann,
H.-A. Wagenknecht* ________ 1904 – 1908

A DNA–Fullerene Conjugate as a Template for Supramolecular Chromophore Assemblies: Towards DNA-Based Solar Cells



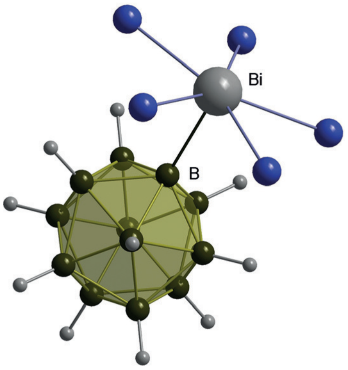
DNA in solar cells: A chromophore assembly of ethynyl Nile red and ethynyl pyrene, templated and ordered by a single-stranded DNA–fullerene conjugates, shows light-harvesting properties and photovoltaic activity. This work demonstrates that DNA is suitable as a structural element for chromophore assemblies in future organic optoelectronic devices, such as solar cells.

B—H Activation

L. W. Zimmermann, N.-D. Van, D. Gudat,
T. Schleid* ________ 1909 – 1911

Bismuth Undecahydro-*closo*-dodecaborane: A Retainable Intermediate of B—H Bond Activation by Bismuth(III) Cations

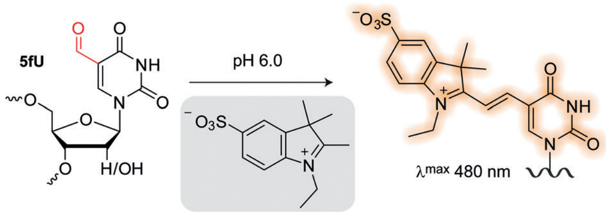
The $[B_{12}H_{12}]^{2-}$ anion manifests a very high stability against metal cations in aqueous solution. Interactions of the soft anion with soft cations via nonclassical hydrogen bonds have been known for a long time. Hydrogen abstraction at the $[B_{12}H_{12}]^{2-}$ cluster by bismuth(III) cations leading to $BiB_{12}H_{11}$ reveals a hitherto unknown and surprising reactivity of this anion.



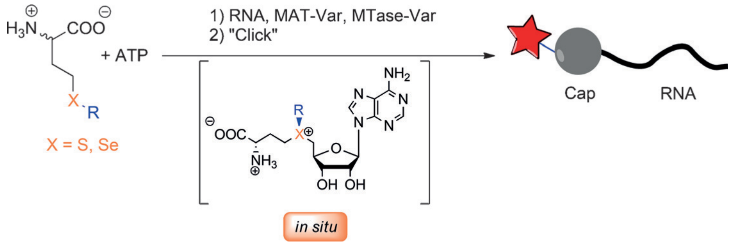
Modified Nucleobases

B. Samanta, J. Seikowski,
C. Höbartner* ________ 1912 – 1916

Fluorogenic Labeling of 5-Formylpyrimidine Nucleotides in DNA and RNA



Shining a light on formylpyrimidines: Mild and orthogonal reaction conditions were established for fluorogenic aldol condensation reactions to generate hemicyanine-like chromophores in DNA and RNA for the residue-specific detection of 5-formyluracil and 5-formylcytosine, which are two naturally occurring oxidized analogues of 5-methylated pyrimidine nucleobases.



Cap in hand: A two-step enzymatic cascade for site-specific mRNA modification has been developed starting from methionine analogues. The approach combines the enzymatic synthesis of AdoMet with modification of the 5′ cap by a specific RNA methyltransferase in one pot. Substrates with, for example, alkene, alkyne, and azido functionalities can be used, which can be further derivatized through click reactions.

mRNA Modification

F. Muttach, A. Rentmeister* 1917 – 1920

A Biocatalytic Cascade for Versatile One-Pot Modification of mRNA Starting from Methionine Analogues

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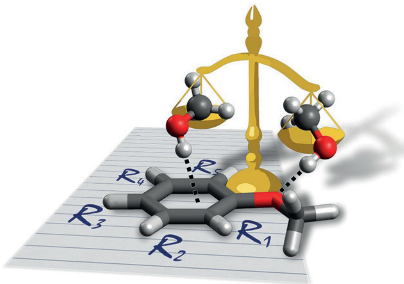
π or O? It's all in the balance! The alkylation pattern of anisole influences the preferred docking site for the OH group of a methanol solvent molecule—at the ether oxygen or the π system of the ring. Vibrational spectroscopy of molecular pairs at low temperature reveals the preferences of this intermolecular balance and provides kJ mol^{-1} quality ratings for quantum chemical predictions.



Aromatic Substitution

VIP

H. C. Gottschalk, J. Altnöder, M. Heger, M. A. Suhm* 1921 – 1924

Control over the Hydrogen-Bond Docking Site in Anisole by Ring Methylation

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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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