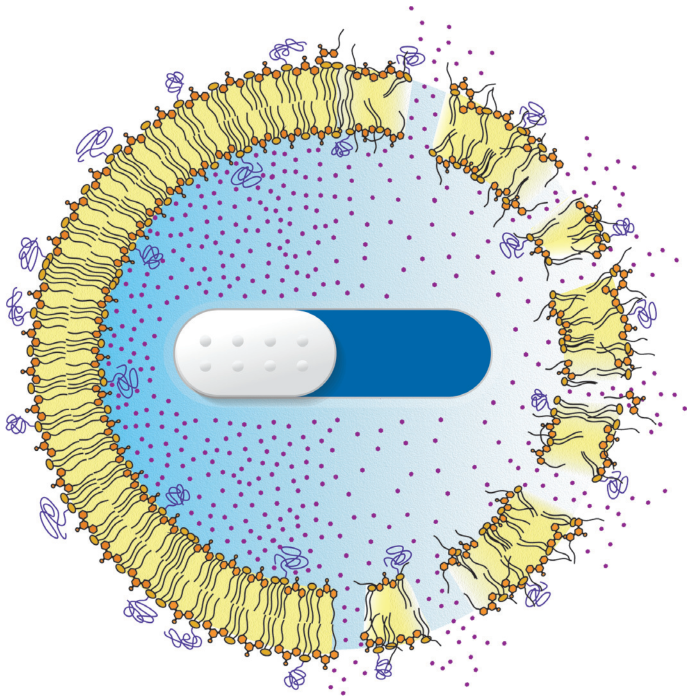
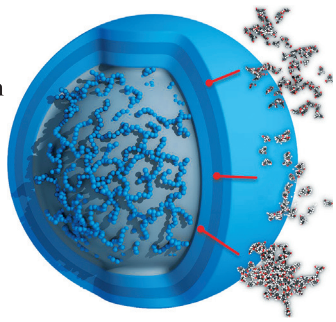
Liposomes ...

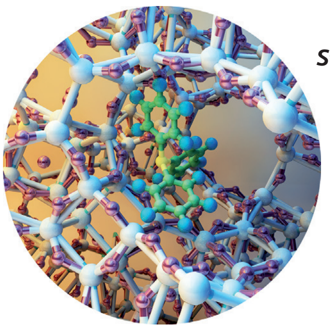


… must protect their cargo during delivery and then release it quickly and selectively at the target site. In their Communication on page 12743 ff., J. Leblond et al. present the development of switchable liposomes that exploit the acidification that occurs after endocytosis. These liposomes are stable for months under physiological conditions and release their content in less than 15 min at acidic pH values. This approach drastically improves drug delivery to the cytosol.

Pseudo-Dendrimers

A polymer core modified with different generation dendrons has properties very similar to those of perfectly branched, high-generation dendrimers. A. Lederer et al. describe this new type of pseudo-dendrimer in their Communication on page 12578 ff.



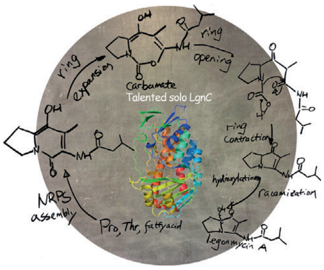


Structure-Directing Agents

In their Communication on page 12805 ff., R. Ryoo and co-workers show the use of organic sulfonium compounds as structure-directing agents for the synthesis of various zeolites, including a germanosilicate zeolite with an open framework structure.

Biosynthesis

In their Communication on page 12697 ff., H. Deng, Y. Yu et al. show that the multifunctional Baeyer–Villiger enzyme LgnC is crucial for the biosynthesis of a class of bacterial pyrrolizidine alkaloids, the so-called legonmycins.



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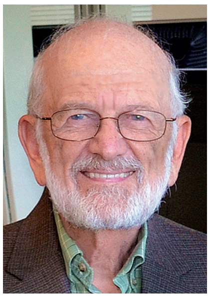
Spotlight on Angewandte's Sister Journals **12540 – 12543**

Author Profile



"My favorite food is "i"-food: Italian, Indian, Indonesian. My favorite music is Wagnerian, especially Parsifal *. ..."* This and more about R. Graham Cooks can be found on page 12548.

R. Graham Cooks **12544 – 12545**

News

P. D. Beer

F. Huang

G. J. L. Bernardes

G. A. Somorjai

Izatt–Christensen Award:
P. D. Beer **12546**

Cram Lehn Pedersen Prize:
F. Huang **12550**

Premio Europeo GE Química Biológica:
G. J. L. Bernardes **12546**

Nichols Medal: G. A. Somorjai **12546**

Books

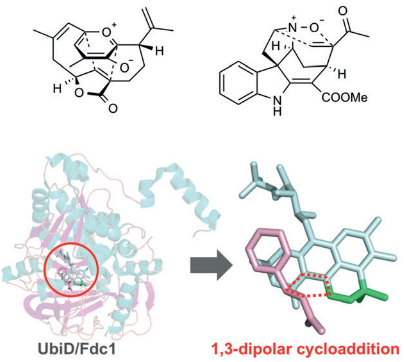
Biocatalysis in Organic Synthesis Kurt Faber, Wolf-Dieter Fessner, Nicholas J. Turner *reviewed by R. Kourist** **12547**

Highlights

Biosynthesis

M. Baunach,
C. Hertweck* ____________ **12550 – 12552**

Natural 1,3-Dipolar Cycloadditions



[3+2] in the wild: Biomimetic natural product syntheses and theoretical considerations have indicated that 1,3-dipolar cycloadditions take place in nature. Now, the structure, biosynthesis, and function of a heavily modified prenylated flavin cofactor have been elucidated. In the azomethine ylide form, it undergoes [3+2] cycloadditions with aromatic acids and promotes their decarboxylation.

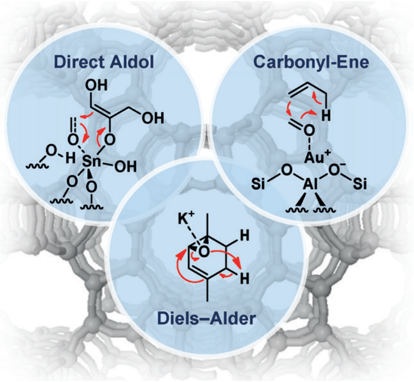
Minireviews

Zeolites

S. Van de Vyver,
Y. Román-Leshkov* ________ **12554 – 12561**

Metalloenzyme-Like Zeolites as Lewis Acid Catalysts for C–C Bond Formation

Yes they can! Metalloenzyme-like zeolites have recently emerged as promising heterogeneous catalysts for C–C bond formation reactions. Progress in their application to direct aldol/retro-aldol, Diels–Alder cycloaddition/dehydration, and carbonyl–ene reactions is reviewed.



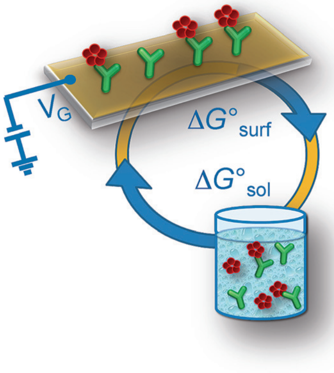
Reviews

Bioanalytics

K. Manoli, M. Magliulo, M. Y. Mulla,
M. Singh, L. Sabbatini, G. Palazzo,
L. Torsi* ____________ **12562 – 12576**

Printable Bioelectronics To Investigate Functional Biological Interfaces

Electrolyte-gated thin-film transistors with integrated protein recognition elements can be used to probe subtle changes occurring in a biolayer. Comparison of the biochemical processes occurring in solution and at the electrode is critical.



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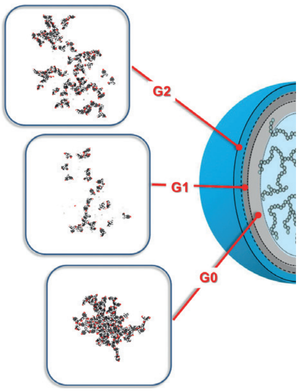
Communications

The generation game: A hyperbranched polymer core modified with different generation dendrons has properties very similar to those of perfectly branched, high-generation dendrimers. The pseudo-dendrimers reveal unique structural confinements that are based on the lower segmental density of the core which is transformed in a smooth and compact nanosphere after modification.

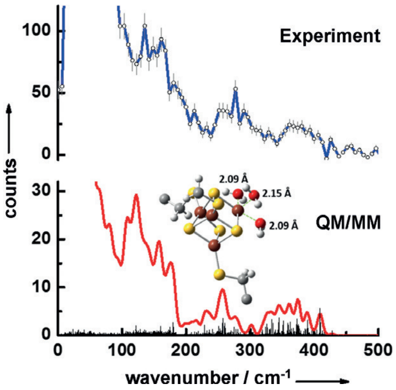


Pseudo-Dendrimers

A. Lederer,* W. Burchard, T. Hartmann, J. S. Haataja, N. Houbenov, A. Janke, P. Friedel, R. Schweins, P. Lindner ______ 12578 – 12583

Dendronized Hyperbranched Macromolecules: Soft Matter with a Novel Type of Segmental Distribution

Frontispiece



Unidentified iron ligands? The comparison of the experimentally obtained nuclear resonance vibrational spectroscopy (NRVS) data of substrate-free LytB with the by QM/MM simulated NRVS data of the substrate-free cluster with different ligands shows the up to now unidentified ligands of substrate-free LytB to be three water molecules (see structure: Fe brown, S yellow, O red).

Enzyme Spectroscopy

I. Faus, A. Reinhard, S. Rackwitz, J. A. Wolny, K. Schlage, H.-C. Wille, A. Chumakov, S. Krasutsky, P. Chaignon, C. D. Poulter, M. Seemann,* V. Schünemann* ______ 12584 – 12587

Isoprenoid Biosynthesis in Pathogenic Bacteria: Nuclear Resonance Vibrational Spectroscopy Provides Insight into the Unusual [4Fe-4S] Cluster of the *E. coli* LytB/IspH Protein

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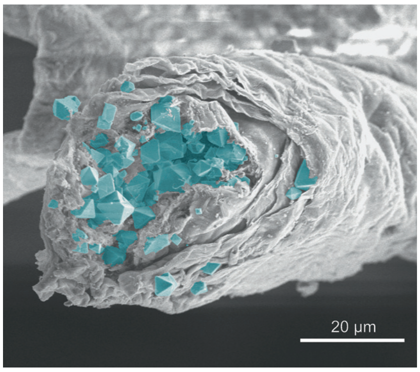


Sponge bag: A composite material is formed from a metal–organic framework (MOF) and a chitin biopolymeric network extracted from a marine sponge. The inner surface functionalities of the biomatrix cause the MOF HKUST-1 (Cu_3BTC_2) to crystalize inside the hollow chitin fibers, resulting in a hierarchical pore system with a surface area of up to 800 $m^2 g^{-1}$. The composite shows a high affinity for toxic industrial gases such as NH_3.

Composite Materials

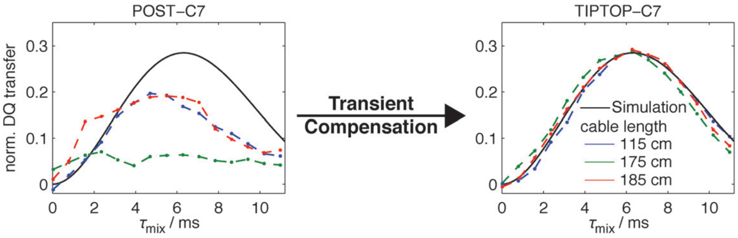
D. Wisser, F. M. Wisser, S. Raschke, N. Klein, M. Leistner, J. Grothe, E. Brunner,* S. Kaskel* ______ 12588 – 12591

Biological Chitin–MOF Composites with Hierarchical Pore Systems for Air-Filtration Applications

Solid-State NMR Spectroscopy

J. J. Wittmann, K. Takeda, B. H. Meier,*
M. Ernst* ———— 12592 – 12596

Compensating Pulse Imperfections in Solid-State NMR Spectroscopy: A Key to Better Reproducibility and Performance



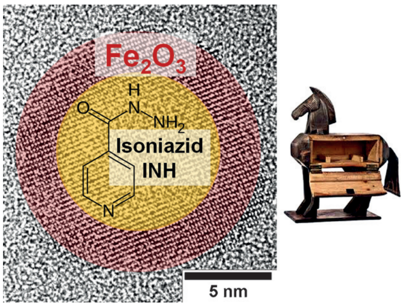
Deviations in the radio-frequency field (pulse transients) can have a severe impact on the performance of pulse sequences. A method based on transient-compensated pulses can greatly improve the efficiency and reproducibility of NMR experiments. The implementation is based on a measurement of the characteristics of the resonance circuit and does not rely on an experimental optimization of the NMR signal.

Tuberculosis

P. Leidinger, J. Treptow, K. Hagens, J. Eich,
N. Zehethofer, D. Schwudke,
W. Oehlmann, H. Lünsdorf, O. Goldmann,
U. E. Schaible,* K. E. J. Dittmar,*
C. Feldmann* ———— 12597 – 12601

Isoniazid@Fe_2O_3 Nanocontainers and Their Antibacterial Effect on Tuberculosis Mycobacteria

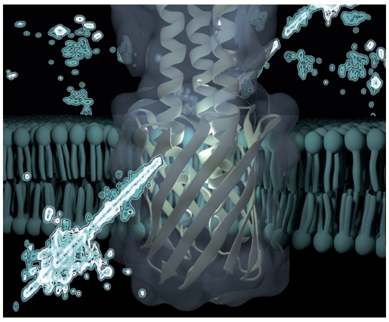
Like a Trojan horse: Isoniazid-filled Fe_2O_3 nanocontainers are actively taken up by tuberculosis-infected macrophages and show high activity against the pathogen *Mycobacterium tuberculosis* (*M.tb.*). This type of container allows a much higher drug loading than other nanocontainer drug-delivery systems, and has a high biocompatibility and biodegradability.



Membrane Proteins

S. A. Shahid, M. Nagaraj, N. Chauhan,
T. W. Franks, B. Bardiaux, M. Habeck,
M. Orwick-Rydmark, D. Linke,*
B.-J. van Rossum* ———— 12602 – 12606

Solid-state NMR Study of the YadA Membrane-Anchor Domain in the Bacterial Outer Membrane

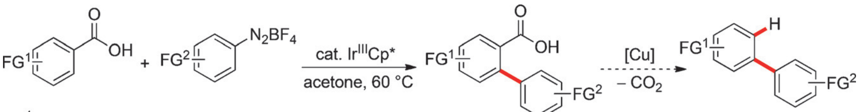


Going native: Solid-state NMR was used to study the structure and dynamics at ambient temperature of the membrane-anchor domain of YadA in a native membrane environment, specifically the outer membrane of *E. coli*. YadA is an adhesin from the pathogen *Yersinia enterocolitica* that is involved in host-cell interactions and is used as a model protein for studying the autotransport process.

C–H Activation

L. Huang, D. Hackenberger,
L. J. Gooßen* ———— 12607 – 12611

Iridium-Catalyzed *ortho*-Arylation of Benzoic Acids with Arenediazonium Salts



FG^1 = I, Ac, COPh, CO_2Me, NO_2, NHAc, etc.
FG^2 = Br, I, Ac, CO_2Me, NHAc, OMe, etc.

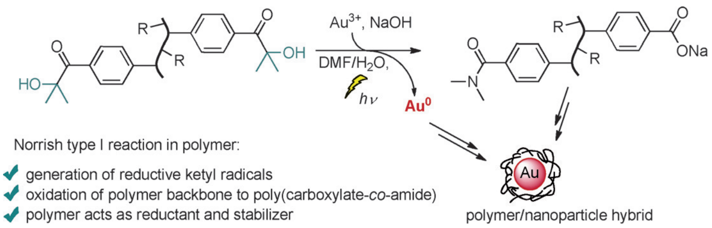
50 examples; 43–92% yield

Directing rather than removed: In the presence of catalytic $[\{IrCp^*Cl_2\}_2]$, benzoic acids react with arenediazonium salts to give the corresponding diaryl-2-carboxylates. If desired, the carboxylate directing group can be removed by in situ protodecarboxylation.

Gold Nanoparticles

F. Mäsing, A. Mardyukov, C. Doerenkamp, H. Eckert, U. Malkus, H. Nüsse, J. Klingauf, A. Studer* 12612–12617

Controlled Light-Mediated Preparation of Gold Nanoparticles by a Norrish Type I Reaction of Photoactive Polymers

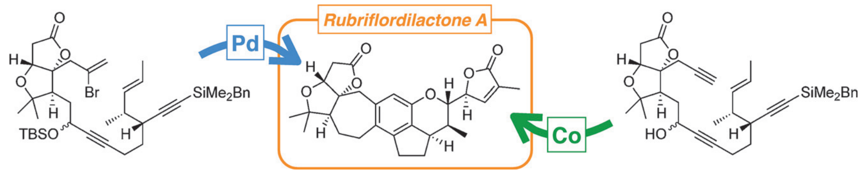


Instant preparation of Au nanoparticles! Mixing a photoactive polymer with $HAuCl_4$ and NaOH in DMF/H_2O and irradiating with light for a few minutes provides stable, spherical, polymer-coated Au nanoparticles with defined diameter. The diameter can be adjusted from 1.5 to 9.6 nm by varying the length and composition of the photoactive polymer.

Natural Product Synthesis

S. S. Goh, G. Chaubet, B. Gockel, M.-C. A. Cordonnier, H. Baars, A. W. Phillips, E. A. Anderson* 12618–12621

Total Synthesis of (+)-Rubriflordilactone A



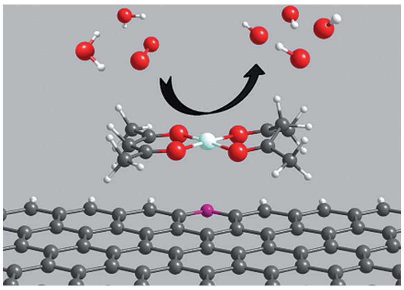
Two in one: Two enantioselective total syntheses of the nortriterpenoid natural product rubriflordilactone A are described, which use palladium- or cobalt-catalyzed cyclizations to converge on a late-stage synthetic intermediate. These key processes are set up through the coupling of a common diyne component with appropriate AB-ring aldehydes, a strategy that enables a broad exploration of this family of natural products, as well as synthetic analogues.

Cobalt Catalysts

J. Han, Y. J. Sa, Y. Shim, M. Choi, N. Park, S. H. Joo,* S. Park* 12622–12626

Coordination Chemistry of [Co(acac)$_2$] with N-Doped Graphene: Implications for Oxygen Reduction Reaction Reactivity of Organometallic Co-O$_4$-N Species

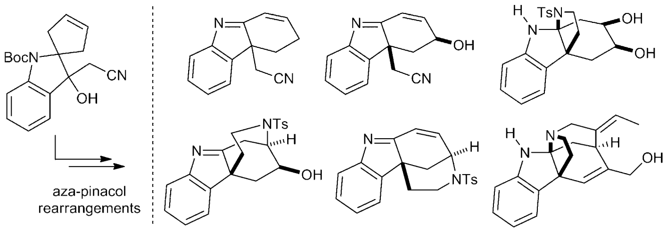
Active species for ORR: Hybrid materials are synthesized by the reaction of a Co-based organometallic complex with N-doped graphene at room temperature. These materials show high electrocatalytic activity for the oxygen reduction reaction. The coordination around Co is revealed by experimental and theoretical studies, and the catalytically active species is identified as a Co-O$_4$-N structure.



Synthetic Methods

Y. Yu, G. Li, L. Jiang, L. Zu* 12627–12631

An Indoxyl-Based Strategy for the Synthesis of Indolines and Indolenines

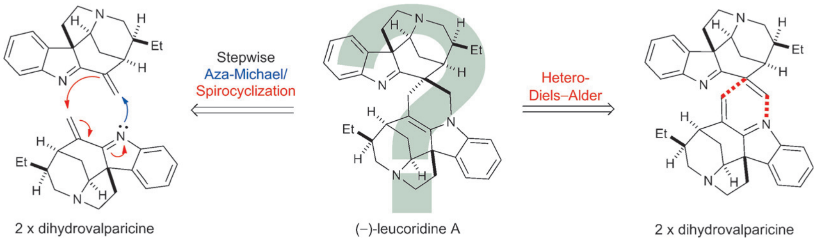


Making other arrangements: The chemical synthesis of a diverse range of functionalized indolines/indolenines and the formal total synthesis of the indoline natural product minfiensine were achieved by using an indoxyl-based strategy that proceeds via unprecedented aza-pinacol rearrangements. This method provides direct access to the core structures of several classes of indole alkaloids by employing conceptually distinct bond disconnections.

Natural Product Synthesis

P. Kokkonda, K. R. Brown, T. J. Seguin, S. E. Wheeler, S. Vaddypally, M. J. Zdilla, R. B. Andrade* ________ 12632 – 12635

Biomimetic Total Syntheses of (−)-Leucoridines A and C through the Dimerization of (−)-Dihydrovalparicine

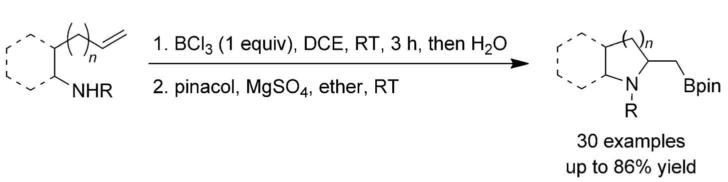


Concise biomimetic syntheses of the *Strychnos-Strychnos*-type bis-indole alkaloids (−)-leucoridine A and C were accomplished through the biomimetic dimerization of (−)-dihydrovalparicine. DFT calculations were used to elucidate the mechanism, which favors a stepwise aza-Michael/spirocyclization sequence over the alternate hetero-Diels–Alder cycloaddition reaction.

Synthetic Methods

C.-H. Yang, Y.-S. Zhang, W.-W. Fan, G.-Q. Liu, Y.-M. Li* ________ 12636 – 12639

Intramolecular Aminoboration of Unfunctionalized Olefins



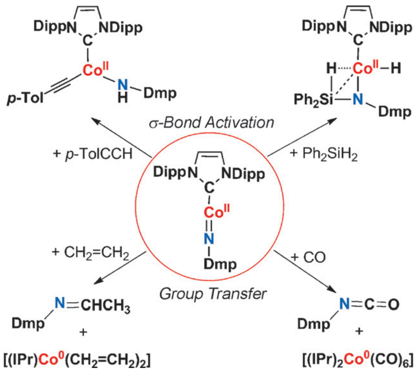
All cats banned! BCl_3 (1 equiv) was used as the sole boron source for the direct intramolecular aminoboration of alkenes. The intramolecular aminoboration of sulfonamide derivatives of 4-penten-1-amines, 5-hexen-1-amines, and 2-allylanilines proceeded readily without a catalyst and was followed by straightforward hydrolysis and treatment with pinacol to give the corresponding boronates (see scheme).

Multiple Bonds

J. Du, L. Wang, M. Xie, L. Deng* ________ 12640 – 12644

A Two-Coordinate Cobalt(II) Imido Complex with NHC Ligation: Synthesis, Structure, and Reactivity

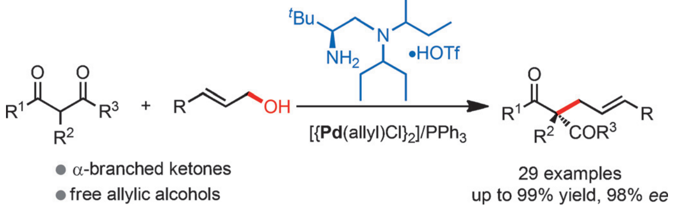
It takes two: A two-coordinate Co complex with a metal–element multiple bond [(IPr)Co(NDmp)] (IPr = 1,3-bis(2′,6′-diisopropylphenyl)imidazole-2-ylidene; Dmp = 2,6-dimesitylphenyl) was prepared and structurally characterized. The low-coordinate Co^{II} complex underwent group-transfer reactions with CO and ethylene, and activated E−H (E = C, Si) bonds to form Co^{II} alkynyl and hydride complexes as 1,2-addition products. Dipp = 2,6-diisopropylphenyl.



Dual Catalysis

H. Zhou, L. Zhang, C. Xu, S. Luo* ________ 12645 – 12648

Chiral Primary Amine/Palladium Dual Catalysis for Asymmetric Allylic Alkylation of β-Ketocarbonyl Compounds with Allylic Alcohols

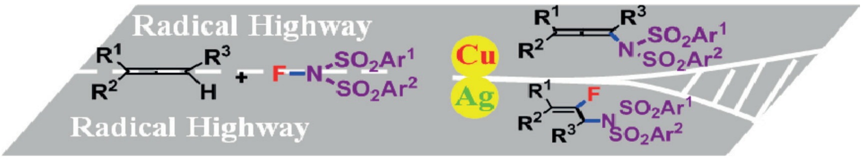


Room to swing two catalysts: A dual catalyst system composed of a chiral primary–tertiary diamine and a palladium complex was developed for the efficient asymmetric allylic alkylation (AAA) of β-ketocarbonyl compounds. This atom-economical process gave acyclic products containing quaternary stereocenters with high enantioselectivity (see scheme; Tf = trifluoromethanesulfonyl).

Allenes

G. Zhang, T. Xiong, Z. Wang, G. Xu,
X. Wang, Q. Zhang* ____ **12649 – 12653**

Highly Regioselective Radical Amination of Allenes: Direct Synthesis of Allenamides and Tetrasubstituted Alkenes

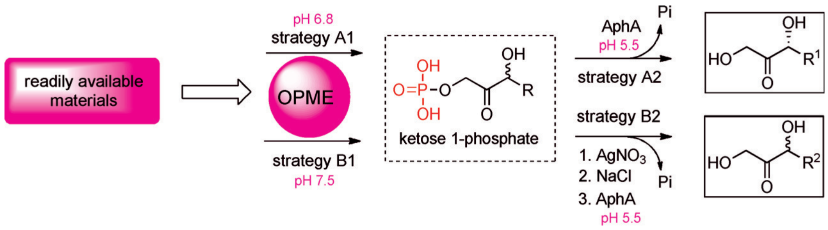


Radical highway: By employing *N*-fluoroarylsulfonimide as a nitrogen source, a facile, mild, and highly regioselective copper-catalyzed oxidative radical amination of various allenes was developed. In addition, a protocol involving nitrogen radical addition/fluorine-atom transfer affords fluorinated tetrasubstituted alkenes by using silver as catalyst.

Monosaccharides

L. Wen, K. Huang, M. Wei, J. Meisner,
Y. Liu, K. Garner, L. Zang, X. Wang, X. Li,
J. Fang, H. Zhang,
P. G. Wang* ____ **12654 – 12658**

Facile Enzymatic Synthesis of Ketoses

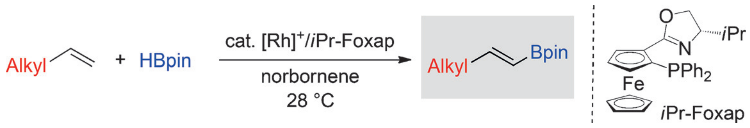


A spoonful of sugar: A convenient, efficient, and cost-effective platform for the facile synthesis of ketoses is described. This method, which involves a one-pot mulitenzyme (OPME) reaction, enables the preparation of rare ketopentoses and ketohexoses from common and inexpensive starting materials with high yield and purity and without the need for a tedious isomer separation step.

Alkenes

M. Morimoto, T. Miura,*
M. Murakami* ________ 12659 – 12663

Rhodium-Catalyzed Dehydrogenative Borylation of Aliphatic Terminal Alkenes with Pinacolborane

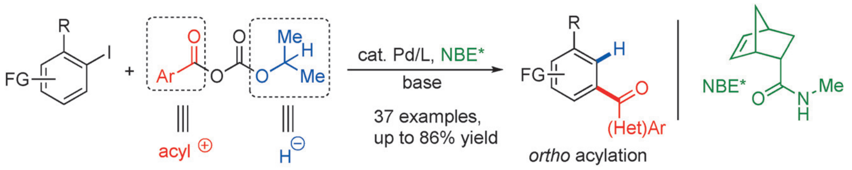


Crazy like a fox: Aliphatic terminal alkenes react with pinacolborane at ambient temperature in the presence of $[Rh(cod)_2]BF_4$/*i*Pr-Foxap and norbornene to produce dehydrogenative borylation compounds as the major product. The reaction is applied to the one-pot syntheses of aldehydes and homoallylic alcohols from aliphatic terminal alkenes. cod = 1,5-cyclooctadiene.

C–H Activation

Z. Dong, J. Wang, Z. Ren,
G. Dong* ________ 12664 – 12668

Ortho C–H Acylation of Aryl Iodides by Palladium/Norbornene Catalysis

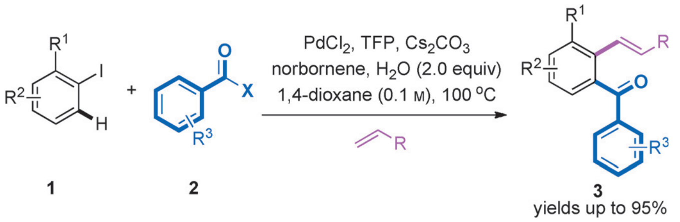


Double (re)agent: A palladium/norbornene-catalyzed *ortho*-acylation of aryl iodides was developed, and is enabled by isopropyl carbonate anhydrides, which function as both an acyl cation equivalent and a hydride source. This reaction exhibits excellent functional-group compatibility and broad substrate scope. Heterocycle moieties can be tolerated on both the aryl and acyl partners. FG = functional group.

Cross-Coupling

Y. Huang, R. Zhu, K. Zhao,
Z. Gu* ________ 12669 – 12672

Palladium-Catalyzed Catellani *ortho*-Acylation Reaction: An Efficient and Regiospecific Synthesis of Diaryl Ketones

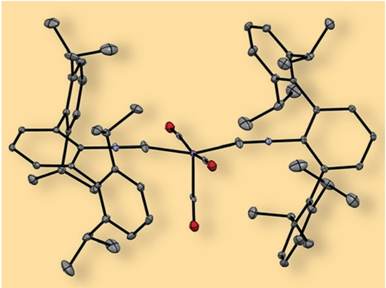


In position: A palladium-catalyzed Catellani *ortho*-acylation of aryl halides using either acid chlorides or acid anhydrides was developed. The reaction efficiently and regiospecifically introduces an acyl group to the position *ortho* to the halogen atom. Preliminary kinetic studies indicate that H_2O plays an important role, and that acid anhydrides might be the active acylating reagents. TFP = tri(2-furyl)phosphine.

Metalloradicals

D. W. Agnew, C. E. Moore,
A. L. Rheingold,
J. S. Figueroa* ________ 12673 – 12677

Kinetic Destabilization of Metal–Metal Single Bonds: Isolation of a Pentacoordinate Manganese(0) Monoradical

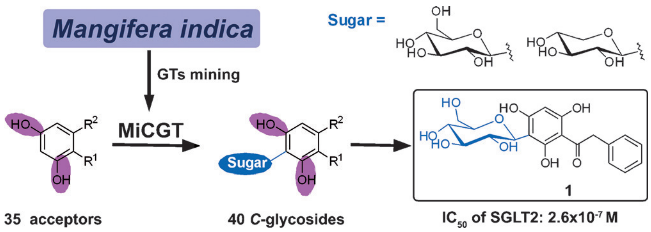


Staying neutral: The unstable 17e⁻ monoradical $[Mn(CO)_5]$ is known to dimerize rapidly to form a Mn–Mn single bond. Two sterically encumbering isocyanide ligands are used to destabilize the Mn–Mn bond, leading to the formation of the isolable manganese(0) monoradical $[Mn(CO)_3(CNAr^{Dipp2})_2]$ (Ar^{Dipp2} = 2,6-(2,6-$iPr_2C_6H_3)_2C_6H_3$). The persistence of this species is exploited to gain insight into nitrosarene spin-trapping studies of $[Mn(CO)_5]$.

Enzyme Catalysis

D. Chen, R. Chen, R. Wang, J. Li, K. Xie,
C. Bian, L. Sun, X. Zhang, J. Liu, L. Yang,
F. Ye, X. Yu, J. Dai* ——— **12678 – 12682**

Probing the Catalytic Promiscuity of a Regio- and Stereospecific C-Glycosyltransferase from *Mangifera indica*

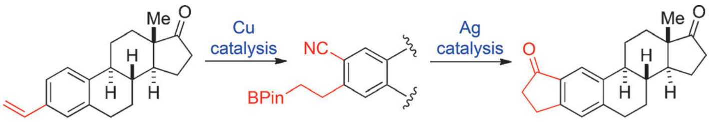


C-glycodiversification: MiCGT, as the first benzophenone C-glycosyltransferase (CGT) from *Mangifera indica*, showed robust regio- and stereospecific C-glycosylation activity for 35 structurally diverse acceptors with UDP-glucose or xylose. The aryl-C-glycoside **1** exhibited potent antidiabetic activity toward SGLT2.

Cyclizations

W. Zhao, J. Montgomery* **12683 – 12686**

Functionalization of Styrenes by Copper-Catalyzed Borylation/*ortho*-Cyanation and Silver-Catalyzed Annulation Processes

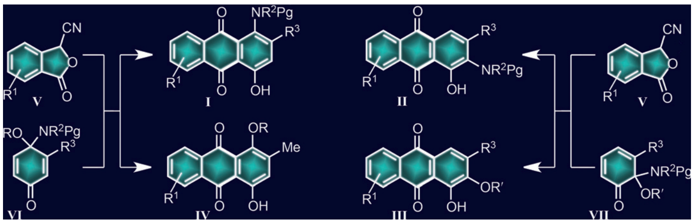


A Cu and Ag sequence: The bis-functionalization of styrenes is accomplished through a copper-catalyzed process that enables hydroboration of the alkene and regioselective *ortho* cyanation of the arene. The resulting adducts are converted, by a radical cyclization process, into a cyclopentanone unit fused to the original aromatic ring. Together, these methods allow efficient cyclopentannulation of a broad range of styrene derivatives.

Anthraquinones

K. C. Nicolaou,* M. Lu, P. Chen,
A. A. Shah ——— **12687 – 12691**

Practical Synthesis of *p*- and *o*-Amino- and Methoxyphenolic Anthraquinones

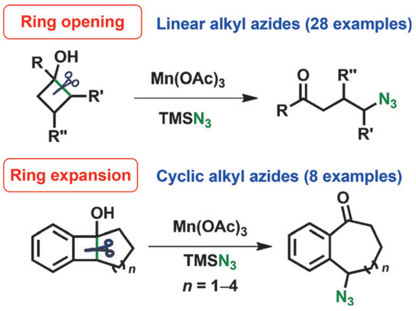


Fusion: 3-Cyanophthalides (**V**) react with substituted amino semiquinone aminals (**VI**, **VII**) under basic conditions to provide selectively a diverse array of substituted amino- and methoxyphenolic anthraquinones (**I**–**IV**).

C–C Activation

R. Ren, H. Zhao, L. Huan,
C. Zhu* ——— **12692 – 12696**

Manganese-Catalyzed Oxidative Azidation of Cyclobutanols: Regiospecific Synthesis of Alkyl Azides by C–C Bond Cleavage



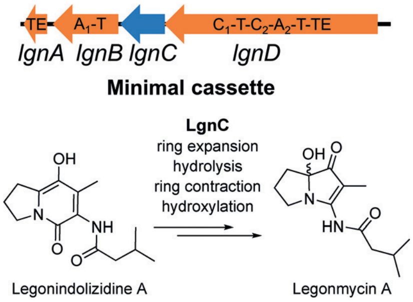
Cleaved: An efficient manganese-catalyzed synthesis of alkyl azides is based on the C–C bond cleavage of cyclobutanols. A wide range of primary, secondary, and tertiary alkyl azides and a series of medium-sized cyclic azides were generated in synthetically useful yields. Preliminary mechanistic studies suggest that the reaction proceeds by a radical mechanism.

Biosynthesis

S. Huang, J. Tabudravu, S. S. Elsayed, J. Travert, D. Peace, M. H. Tong, K. Kyeremeh, S. M. Kelly, L. Trembleau, R. Ebel, M. Jaspars, Y. Yu,* H. Deng* ____ **12697 – 12701**

Discovery of a Single Monooxygenase that Catalyzes Carbamate Formation and Ring Contraction in the Biosynthesis of the Legonmycins

Back Cover

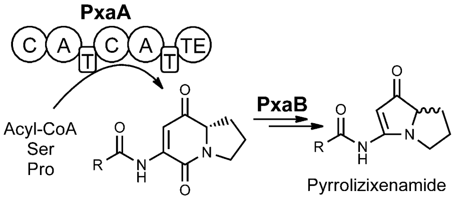


Solo performance: The legonmycins, new bacterial pyrrolizidine alkaloids, are assembled by a non-ribosomal peptide synthetase. The multifunctional FAD-containing enzyme LgnC catalyzes the transformation of indolizidine intermediates into pyrrolizidines by carbamate formation, followed by hydrolysis, decarboxylation-driven ring contraction, and hydroxylation as the crucial steps of legonmycin biosynthesis.

Biosynthesis

O. Schimming, V. L. Challinor, N. J. Tobias, H. Adihou, P. Grün, L. Pöschel, C. Richter, H. Schwalbe, H. B. Bode* ____ **12702 – 12705**

Structure, Biosynthesis, and Occurrence of Bacterial Pyrrolizidine Alkaloids

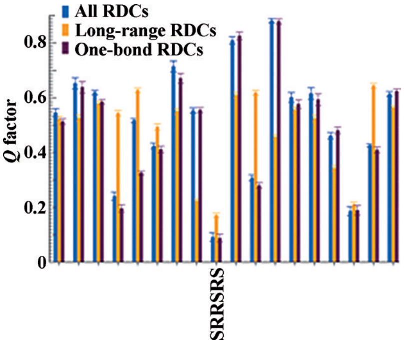


The structures of bacterial pyrrolizidine alkaloids from *Xenorhabdus*, the pyrrolizixenamides, have been elucidated by two-dimensional NMR spectroscopy and mass spectrometry. Their biosynthesis is shown to involve the bimodular non-ribosomal peptide synthetase PxaA and the unique monooxygenase PxaB.

NMR Spectroscopy

N. Nath, E. J. d'Auvergne, C. Griesinger* ____ **12706 – 12710**

Long-Range Residual Dipolar Couplings: A Tool for Determining the Configuration of Small Molecules

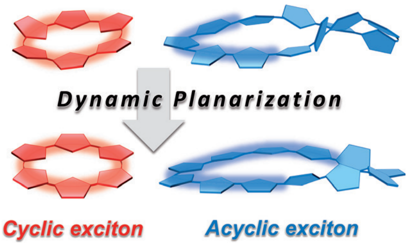


Rewarding long-distance relationships: Long-range residual dipolar couplings (RDCs) between protons and remote carbon atoms complement one-bond RDCs in conveying NMR spectroscopic information about the three-dimensional structure of molecules in solution. The use of long-range RDCs in conjunction with one-bond RDCs showed, on the basis of the quality (Q) factor, that the correct diastereomer of strychnine had the *SRRSRS* configuration (see graph).

Photophysics

K. H. Park, P. Kim, W. Kim, H. Shimizu, M. Han, E. Sim,* M. Iyoda,* D. Kim* ____ **12711 – 12715**

Excited-State Dynamic Planarization of Cyclic Oligothiophenes in the Vicinity of a Ring-to-Linear Excitonic Behavioral Turning Point



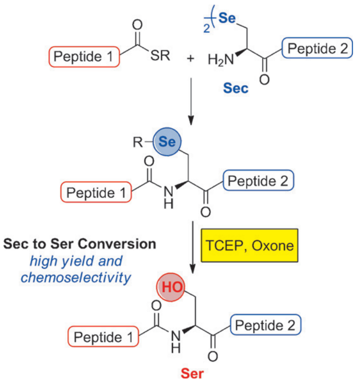
Going around in circles: Excited-state dynamic planarization processes of π-conjugated cyclic oligothiophenes were investigated using time-resolved fluorescence spectra and molecular dynamics simulations. Excitons formed in a cyclic oligothiophene composed of six subunits fully delocalize ("cyclic exciton"), whereas those formed in larger systems fail to achieve complete delocalization ("acyclic exciton").

Protein Ligation

L. R. Malins, N. J. Mitchell, S. McGowan,
R. J. Payne* ——— 12716 – 12721

Oxidative Deselenization of Selenocysteine: Applications for Programmed Ligation at Serine

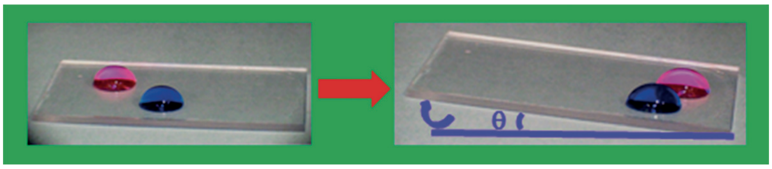
An operationally simple method for the rapid and chemoselective conversion of selenocysteine (Sec) to serine (Ser) in aqueous media is described. This mechanistically distinct transformation at selenium facilitates the synthesis of complex peptides and proteins, as highlighted in the synthesis of fragments of the epithelial glycoproteins MUC5AC and MUC4 and in the total synthesis of the serine protease inhibitor eglin C.



Coatings

M. Rabnawaz, G. Liu,*
H. Hu ——— 12722 – 12727

Fluorine-Free Anti-Smudge Polyurethane Coatings



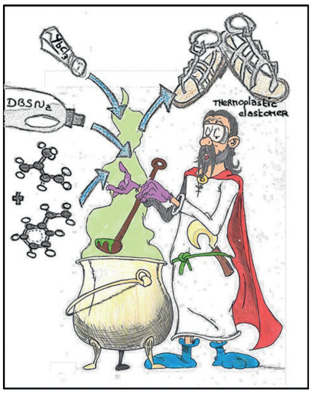
Wear and tear without a smear: Anti-smudge polyurethane coatings produced without fluorinated reagents were clear at thicknesses up to tens of micrometers. The coatings were applied to a diverse range of substrates and shown to repel ink, a fingerprint liquid, paint, and water. Moreover, they retained their anti-smudge properties even after extensive wear.

Heterogeneous Catalysis

I. V. Vasilenko, H. Y. Yeong, M. Delgado,
S. Ouardad, F. Peruch, B. Voit,
F. Ganachaud,*
S. V. Kostjuk* ——— 12728 – 12732

A Catalyst Platform for Unique Cationic (Co)Polymerization in Aqueous Emulsion

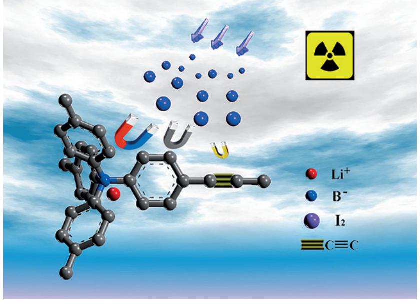
Old pot, best cooking! Well-known hyperbranched anionic surfactants (hard DBSNa) mixed together with rare earth metal salts, generate Lewis acid surfactant complexes. These complexes show remarkable efficiency in the (co)polymerization of, for example, styrene and isoprene into long and linear chains.



Porous Aromatic Frameworks

Z. Yan, Y. Yuan, Y. Tian, D. Zhang,
G. Zhu* ——— 12733 – 12737

Highly Efficient Enrichment of Volatile Iodine by Charged Porous Aromatic Frameworks with Three Sorption Sites

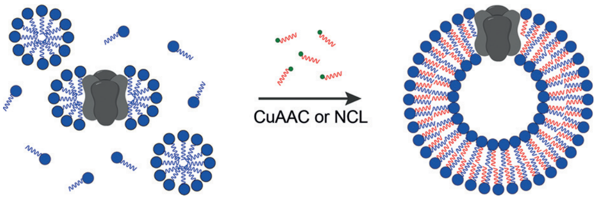


Polymers for iodine capture: Targeted synthesis of porous aromatic frameworks has been achieved by choosing the monomer lithium tetrakis(4-iodophenyl)borate (LTIPB) as the building block. Three effective sorption sites are assembled into the frameworks: an aromatic ring, triple bond, and ionic bond. These frameworks exhibit the highest values for iodine sorption among all porous materials (zeolites, MOFs, and POFs).

Membrane Proteins

C. M. Cole, R. J. Brea, Y. H. Kim,
M. D. Hardy, J. Yang,
N. K. Devaraj* ———— **12738 – 12742**

Spontaneous Reconstitution of Functional Transmembrane Proteins During Bioorthogonal Phospholipid Membrane Synthesis



Membrane Proteins Inc.: The spontaneous reconstitution of functional integral membrane proteins (gray) during the de novo synthesis of biomimetic phospholipid bilayers is described. The method takes advantage of bioorthogonal coupling reactions for the non-enzymatic generation of proteoliposomes from micelle-solubilized proteins. This chemoselective approach results in a fast and clean reconstitution without the need for dialysis to remove excess detergent.

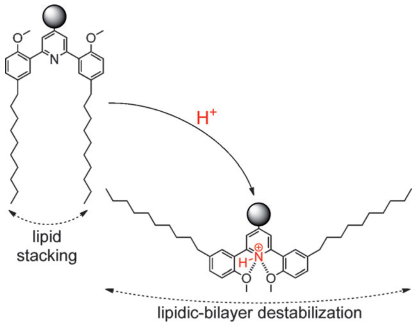
Drug Delivery

W. Viricel, A. Mbarek,
J. Leblond* ———— **12743 – 12747**

Switchable Lipids: Conformational Change for Fast pH-Triggered Cytoplasmic Delivery

Front Cover

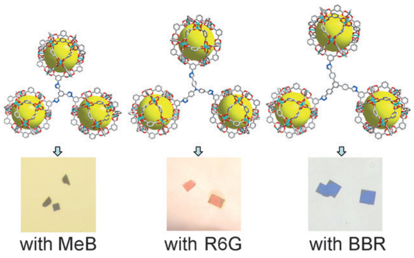
Switch it on! The integration of pH-sensitive switchable lipids (see picture) into poly(ethylene glycol)-coated liposome formulations enabled the efficient cytoplasmic delivery of polar compounds through an endosomal-escape mechanism. The liposome formulations containing the switchable lipids were stable at pH 7.4 and upon storage but instantly destabilized at endosomal pH values (pH 5–5.5).



Large-Molecule Adsorption

P.-Z. Li, X.-J. Wang, S. Y. Tan, C. Y. Ang,
H. Chen, J. Liu, R. Zou,*
Y. Zhao* ———— **12748 – 12752**

Clicked Isoreticular Metal–Organic Frameworks and Their High Performance in the Selective Capture and Separation of Large Organic Molecules

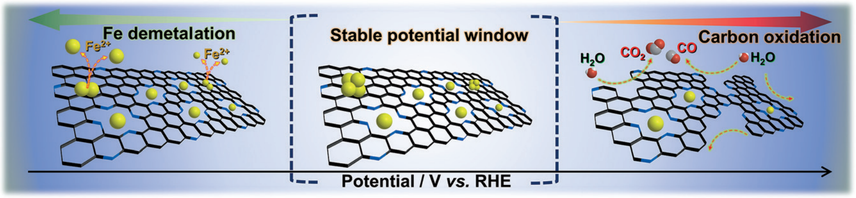


Color me pretty: Highly porous metal–organic frameworks with uniform topological networks were constructed by isoreticular extension through click reactions. The accessibility of their pores to large molecules make them highly promising materials for size-dependent large-molecule capture and separation, as demonstrated visually by the selective capture of dye molecules (see picture; MeB = methylene blue, R6G = rhodamine 6G, BBR = brilliant blue R).

Electrocatalysis

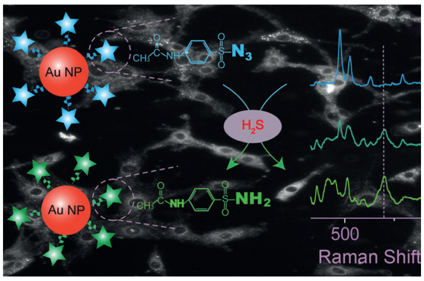
C. H. Choi,* C. Baldizzone, J.-P. Grote,
A. K. Schuppert, F. Jaouen,*
K. J. J. Mayrhofer* ———— **12753 – 12757**

Stability of Fe-N-C Catalysts in Acidic Medium Studied by Operando Spectroscopy



The stable potential window of Fe-N-C catalysts for oxygen reduction reactions is studied using a scanning flow cell equipped with advanced online analytical techniques. Fe demetalation and carbon oxidation (see picture) are observed in low (< 0.7 V) and high (> 0.9 V) potential regions, respectively, which can introduce significant performance drops in a fuel cell.

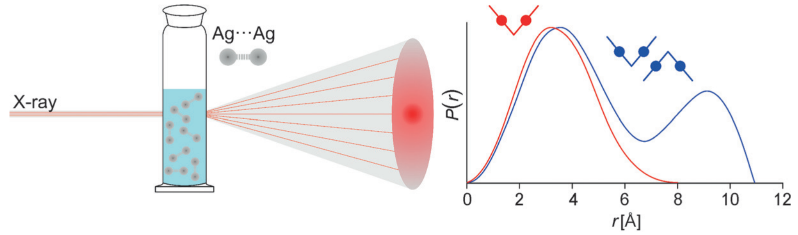
Rapid, selective, and sensitive: The endogenous H_2S in living cells can be detected rapidly, selectively, and sensitively using a surface-enhanced Raman scattering (SERS) nanosensor, 4-acetamidobenzenesulfonyl azide-functionalized gold nanoparticles (AuNPs/4-AA). Based on the rapid and specific reaction between H_2S and 4-AA, combined with the sensitive fingerprinting capability of SERS, the nanosensor can monitor the endogenous H_2S generated in a variety of pathophysiological pathways.



H_2S Nanosensors

D. W. Li,* L. L. Qu, K. Hu, Y. T. Long,*
H. Tian ______ **12758 – 12761**

Monitoring of Endogenous Hydrogen Sulfide in Living Cells Using Surface-Enhanced Raman Scattering

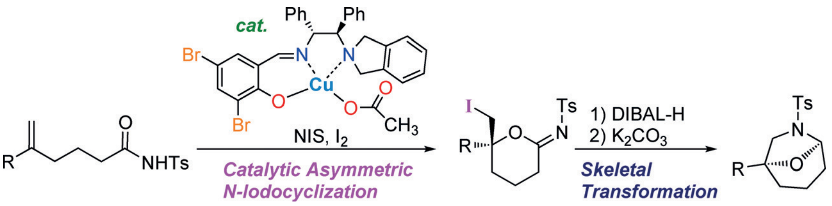


In close quarters: Small-angle X-ray scattering (SAXS) is used to identify structure in solution by taking advantage of the excellent scattering intensity of heavy metals which have associated through metallophilic interactions. The close relationship between the solid-state and solution arrangements of a $[Ag_2(bisNHC)_2]^{2+}$ system is described.

Metal–Metal Interactions

A. Cebollada, A. Vellé, M. Iglesias,
L. B. Fullmer, S. Goberna-Ferrón,
M. Nyman,*
P. J. Sanz Miguel* ______ **12762 – 12766**

Direct X-Ray Scattering Evidence for Metal–Metal Interactions in Solution at the Molecular Level



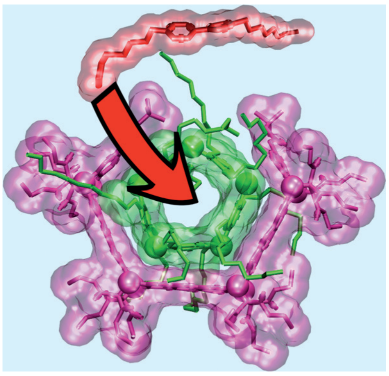
An aminoiminophenoxy copper carboxylate-catalyzed asymmetric iodocyclization of *N*-Tosyl alkenamides gave *O*-cyclized products in good yields with high enantioselectivity. Chiral 8-oxa-6-azabicyclo[3.2.1]octanes were synthesized by a sequential reduction/cyclization process from the iodocyclization product. DFT calculations suggested that the *N*-tosyl alkenamides are activated by hydrogen bonding with a carboxylate anion on the copper center to allow iodo-*O*-cyclization.

Aymmetric Iodocyclization

T. Arai,* O. Watanabe, S. Yabe,
M. Yamanaka ______ **12767 – 12771**

Catalytic Asymmetric Iodocyclization of *N*-Tosyl Alkenamides using Aminoiminophenoxy Copper Carboxylate: A Concise Synthesis of Chiral 8-Oxa-6-Azabicyclo[3.2.1]octanes

Hosts turn into guests in the presence of preorganized, C-shaped molecular strips. Such structures can now be readily built by chirality-assisted synthesis. They embrace pillararene macrocycles in a specific binding mode that is driven by π–π stacking and solvophobic interactions. This action in turn regulates the affinity of the macrocycles for binding electron-deficient guests in a cooperative fashion.



Shape Control

X. Liu, Z. J. Weinert, M. Sharafi, C. Liao,
J. Li,* S. T. Schneebeli* ___ **12772 – 12776**

Regulating Molecular Recognition with C-Shaped Strips Attained by Chirality-Assisted Synthesis

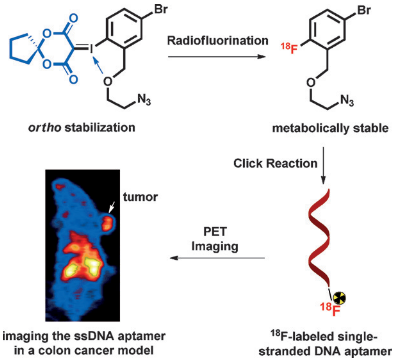
Inside Cover

Imaging Agents

L. Wang, O. Jacobson, D. Avdic,
B. H. Rotstein, I. D. Weiss, L. Collier,
X. Chen,* N. Vasdev,*
S. H. Liang* ______________ **12777 – 12781**

Ortho-Stabilized ^{18}F-Azido Click Agents and their Application in PET Imaging with Single-Stranded DNA Aptamers

Markedly apt: A high-yielding direct radiofluorination strategy via *ortho*-oxygen-substituted iodonium derivatives is described. A ssDNA aptamer (sgc8), labelled with the resulting ^{18}F azido agent through click chemistry, was used for PET imaging and provides the first example for the noninvasive in vivo PET imaging of protein tyrosine kinase 7 (PTK-7).

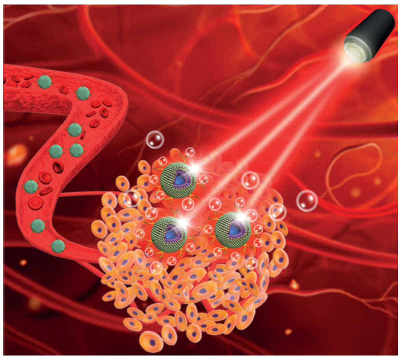


Anticancer Nanoparticles

J. Shao, M. Xuan, L. Dai, T. Si, J. Li,*
Q. He* ______________ **12782 – 12787**

Near-Infrared-Activated Nanocalorifiers in Microcapsules: Vapor Bubble Generation for In Vivo Enhanced Cancer Therapy

Antitumor bubbles: A photothermal theranostic platform based on biocompatible gold nanorod-assembled capsules was demonstrated with good deformability behavior and behavior similar to red blood cells. The resulting vapor bubbles, induced by a cumulative thermal effect between adjacent gold nanorods, can locally damage tumor cells and enable photothermal therapy with high efficacy compared to single gold nanorods.

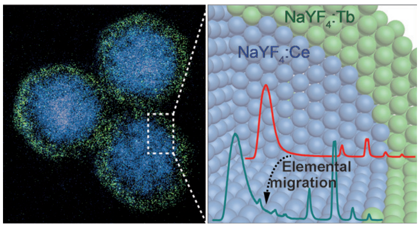


Core–Shell Nanostructures

B. Chen, D. Peng, X. Chen, X. Qiao, X. Fan,
F. Wang* ______________ **12788 – 12790**

Establishing the Structural Integrity of Core–Shell Nanoparticles against Elemental Migration using Luminescent Lanthanide Probes

Border control: The diffusion of dopant ions in core–shell nanostructures is detected using luminescent lanthanide probes (Ce^{3+} and Tb^{3+}). Core–shell nanoparticles synthesized by a wet-chemistry route retain high structural integrity and after annealing at elevated temperatures, migration of elements across the core–shell interface is detected.

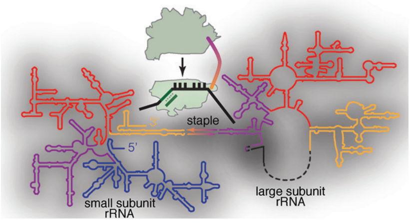


Orthogonal Translation

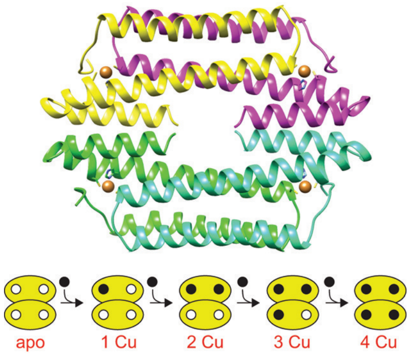
S. D. Fried, W. H. Schmied,
C. Uttamapinant,
J. W. Chin* ______________ **12791 – 12794**

Ribosome Subunit Stapling for Orthogonal Translation in *E. coli*

Stapling the ribosome together: An orthogonal ribosome was designed in which the large and small subunits are connected through a covalent RNA staple, and directed to an orthogonal mRNA. This ribosome is active in protein synthesis in cells and enables otherwise lethal mutations to be introduced into the large subunit. This paves the way for the ribosome-catalyzed synthesis of unnatural polymers by cellular orthogonal translation.



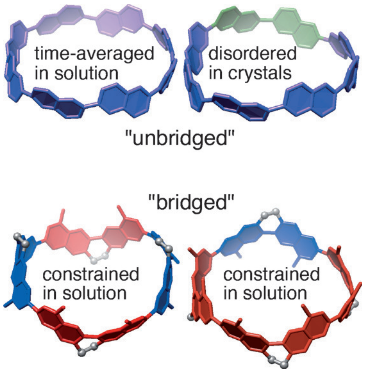
Working together: The stepwise cooperativities of Cu binding to the homotetrameric copper-sensitive operon repressor (CsoR) were resolved by mass spectrometry, with the extent of cooperativity related to gas phase properties. The gas phase holo (Cu_4) structure was found to favor a more compact state, and was markedly more resistant to fragmentation than apo- or partially Cu-ligated species.



Structural Biology

A. D. Jacobs, F.-M. J. Chang, L. Morrison, J. M. Dilger, V. H. Wysocki, D. E. Clemmer, D. P. Giedroc* ———— **12795 – 12799**

Resolution of Stepwise Cooperativities of Copper Binding by the Homotetrameric Copper-Sensitive Operon Repressor (CsoR): Impact on Structure and Stability

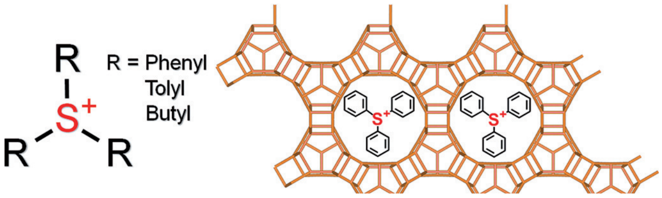


Being persistent: Cyclonaphthylene nanohoops have been synthesized and characterized in solution and in the solid state. The naphthylene units in [8]cyclo-*amphi*-naphthylene, prepared by linking naphthylene units at the 2,6-positions, can undergo rotation, but rigidification with the aid of methylene bridges affords persistent molecular structures in solution.

Cycloarylenes

Z. Sun, P. Sarkar, T. Suenaga, S. Sato, H. Isobe* ———— **12800 – 12804**

Belt-Shaped Cyclonaphthylenes



A zeolite with MEL structure and three other germanosilicate zeolites were synthesized using organic sulfonium compounds as structure-directing agents. Depending on the synthesis conditions, the germanosilicates had ISV, ITT, or a new zeolite structure. The new germanosilicate exhibited two types of accessible micropores with diameters of 0.61 and 0.78 nm after calcination.

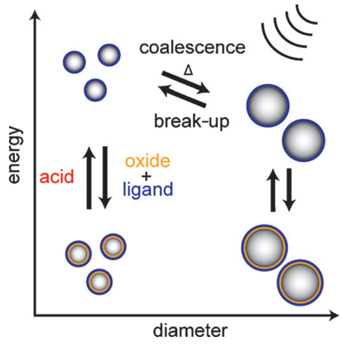
Structure-Directing Agents

C. Jo, S. Lee, S. J. Cho, R. Ryoo* ———— **12805 – 12808**

Synthesis of Silicate Zeolite Analogues Using Organic Sulfonium Compounds as Structure-Directing Agents

Inside Back Cover

An ultrasonication method for reversibly changing the size of gallium nanoparticles (GaNPs) has been developed. By changing the temperature or adding acid, the balance between the break-up and coalescence of the GaNPs can be adjusted by modulating the natural surface oxide layer and the stabilizing effect of a surfactant. Moreover, these GaNPs display size-dependent plasmonic absorption.



Nanoparticles

A. Yamaguchi,* Y. Mashima, T. Iyoda ———— **12809 – 12813**

Reversible Size Control of Liquid-Metal Nanoparticles under Ultrasonication

Metathesis

A. D. Lackner,
A. Fürstner* ____________ 12814–12818

The Triple-Bond Metathesis of Aryldiazonium Salts: A Prospect for Dinitrogen Cleavage

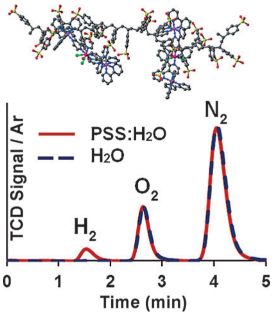
Who knows? Although the extrusion of molecular nitrogen from aryldiazonium salts is extremely facile, the metathetic cleavage of the N—N triple bond on treatment with alkylidyne ate complexes of molybdenum or tungsten is shown to be even faster. The analogy between $[Ar-N_2]^+$ and known $[M-N_2]$ complexes makes this process a potential model for dinitrogen cleavage devoid of any redox steps.

Photocatalysis

T. R. Canterbury, S. M. Arachchige,
R. B. Moore,*
K. J. Brewer ____________ 12819–12822

Increased Water Reduction Efficiency of Polyelectrolyte-Bound Trimetallic [Ru,Rh,Ru] Photocatalysts in Air-Saturated Aqueous Solutions

Better together: A photocatalytic system that functions under aerobic conditions by electrostatically binding water reduction photocatalysts to poly(4-styrenesulfonate) (PSS) is reported. The water-soluble complex–PSS assemblies were formed in situ upon addition of PSS to the photocatalyst solutions. Substantial H_2 production under aerobic conditions occured for PSS-containing aqueous solutions (see picture).



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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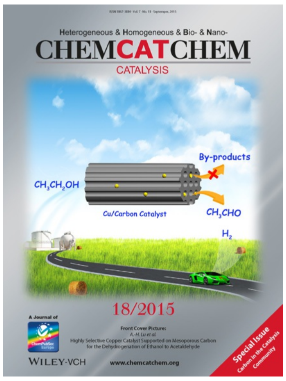
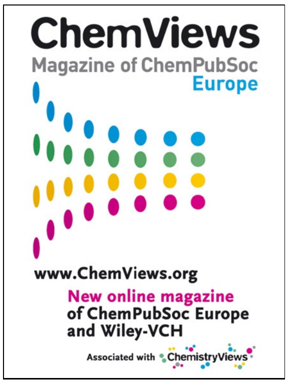




Angewandte Corrigendum

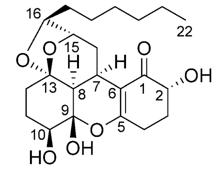
Stereocontrolled Synthesis of Trichodermatide A

H. Shigehisa, Y. Suwa, N. Furiya,
Y. Nakaya, M. Fukushima, Y. Ichihashi,
K. Hiroya* ______________ **3646–3649**

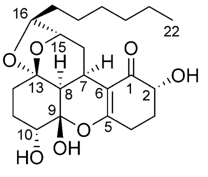
Angew. Chem. Int. Ed. **2013**, *52*

DOI: 10.1002/anie.201210099

A publication by the Trauner group[1] prompted the authors of this Communication to make structural assignments by re-examination of the NMR experiments for synthetic trichodermatide A: NOESY correlations between H10 and OH9, and between H8 and OH10, were observed. Furthermore, the coupling constant (6.8 Hz) derived from the protons at C7 and C8 indicated a *cis* relationship. Therefore, the configuration of the actual structure of trichodermatide A in Figure 1 should be **1**′. The structure **1**′ is also strongly supported by the additional experiments.[2] With the above correction, compounds **17** and **22** in Scheme 3 and compounds **23**, **24**, **25**, and **26** in Scheme 4 should be revised in the same way with regard to the stereochemical configuration at C10.



originally assigned structure of trichodermatide A (**1**)



revised structure (**1'**)

The sentence “The diastereomer of **17** (C10-α-OH) was not detected because the α face the C8–C9 olefin is probably shielded by the axially oriented C13–α-O ether bond” should be corrected as “The diastereomer of **17** (C10–β-OH) was not detected probably because of the stereoelectronically required axial α-allylic C–H bond”. The sentence “The stereochemistry of the C9 hydroxy group is fixed at the β position by intramolecular hydrogen bonding with C10–β-OH because of its hemiketal character” should be corrected as “... by plausible intramolecular hydrogen bonding with the C13–β-O ether ...”. The total synthesis of trichodermatide A stands as reported.

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[1] E. Myers, E. Herrero-Gomez, I. Albrecht, J. Lachs, P. Mayer, M. Hanni, C. Ochsenfeld, D. Trauner, *J. Org. Chem.* **2014**, *79*, 9812.

[2] Unpublished results, manuscript in preparation.

Angewandte Corrigendum

Stereoselective Retentive Domino Transmetalations of Secondary Alkyllithium Compounds to Functionalized Secondary Alkylcopper Reagents

K. Moriya, M. Simon, R. Mose,
K. Karaghiosoff,
P. Knochel* ___________ **10963–10967**

Angew. Chem. Int. Ed. **2015**, *54*

DOI: 10.1002/anie.201505740

In Table 3 of this Communication on page 10965 the electrophiles E appear in the wrong order. The electrophile for entries 1 and 2 should be **7g** (allyl chloride), and the electrophile for entries 3 and 4 should be **7d** (ethylene oxide).

Angewandte Corrigendum

Nitrile–Nitrile C–C Coupling at Group 4 Metallocenes to Form 1-Metalla-2,5-diaza-cyclopenta-2,4-dienes: Synthesis and Reactivity

L. Becker, P. Arndt, H. Jiao,
A. Spannenberg,
U. Rosenthal* ________ **11396–11400**

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

DOI: 10.1002/anie.201303748

In the DFT calculations part of this Communication (p. 11398, left column, last paragraph) the calculated values for the formation free energies of $[\mathrm{Cp}^*_2\mathrm{M}(\mathrm{NCPh})_2]$ (M = Ti, Zr) (from **1-Ti** and **1-Zr**) and of **2a-M** (from **1-M**) are wrong. The corrected text paragraph is as follows:

"For the substitution of the alkyne ligand in **1-Ti** and **1-Zr** by two PhCN molecules to $[\mathrm{Cp}^*_2\mathrm{Ti}(\mathrm{NCPh})_2]$ and $[\mathrm{Cp}^*_2\mathrm{Zr}(\mathrm{NCPh})_2]$ (Scheme 4), the computed reaction energy is highly exergonic by 26.1 and 23.4 kcal mol^{-1}, respectively, indicating their thermodynamic probability. For the C–C coupling of two nitrile units in $[\mathrm{Cp}^*_2\mathrm{M}(\mathrm{NCPh})_2]$, we have located the authentic transition states $[\mathrm{Cp}^*_2\mathrm{M}(\mathrm{NCPh})_2\text{-TS}]$, and the computed free energy barrier is 10.3 kcal mol^{-1} for M = Ti and 9.6 kcal mol^{-1} for M = Zr. The formation of **2a-Ti** (-1.6 kcal mol^{-1}) and **2a-Zr** (-3.6 kcal mol^{-1}) is exergonic. These very low exergonic energy shows the thermodynamic probability of the reverse reaction from **2a-M** back to $[\mathrm{Cp}^*_2\mathrm{M}(\mathrm{NCPh})_2]$ (the barrier of the reverse reaction is 11.9 and 13.2 kcal mol^{-1} for **2a-Ti** and **2a-Zr**, respectively), and also a possible equilibrium between **2a-M** and $[\mathrm{Cp}^*_2\mathrm{M}(\mathrm{NCPh})_2]$. The total reaction free energy from **1-Ti** to **2a-Ti** is -27.7 kcal mol^{-} and from **1-Zr** to **2a-Zr** -27.0 kcal mol^{-1}."

The general conclusions are not affected by the changes in the values.

Angewandte Addendum

The Retro-Hydroformylation Reaction

S. Kusumoto, T. Tatsuki,
K. Nozaki* ____________ **8458–8461**

Angew. Chem. Int. Ed. **2015**, *54*

DOI: 10.1002/anie.201503620

Following publication of this Communication, Dr. Boy Cornils (Hofheim, Germany) kindly informed the authors about the missing references for the retro-hydroformylation reaction. In the late 1960s, Orlicek[1] and inventors from Ruhrchemie AG[2] reported that cracking of isobutyraldehyde into propylene, carbon monoxide, and hydrogen was possible. The work was also published in academic literature in 1972.[3] In this reference, the two authors reported about the cracking of isobutyraldehyde, an undesired side-product of the oxo-process, to recover propylene and syngas using rhodium on alumina as a catalyst.

Dr. Cornils comments that in 1972, his group confirmed the data in a months-and-months run on a pilot plant scale. He says "it worked but not economically enough for industrial scale application."

In addition, in 1968, Tsuji et al. reported the formation of nonene as a major product in their attempt for decarbonylation of decanal with a heterogeneous palladium catalyst.[4]

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[1] A. Orlicek, Austrian Patent 277.949 (1968).

[2] J. Falbe, H. D. Hahn, H. Tummes, DE 1.668.647, 1.767.281, 1.809.727, and 1.917.244 (1968–1970).

[3] J. Falbe, H. D. Hahn, *Chemiker-Zeitung* **1972**, *96*, 164.

[4] J. Tsuji, K. Ohno, *J. Am. Chem. Soc.* **1968**, *90*, 94.