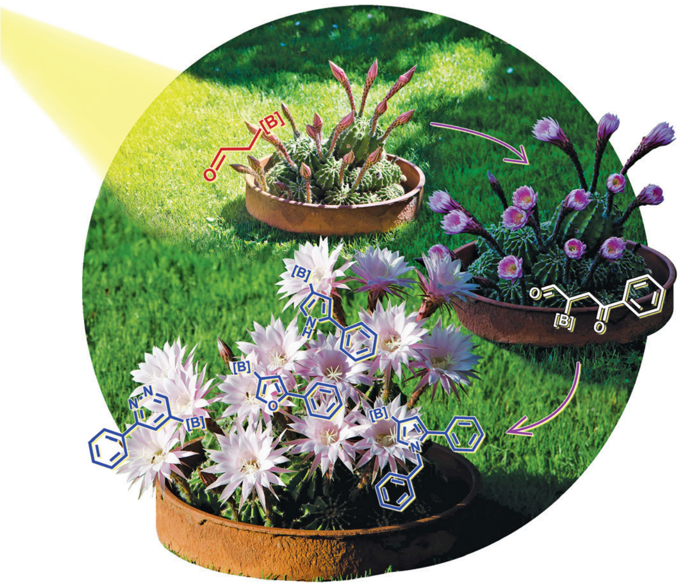
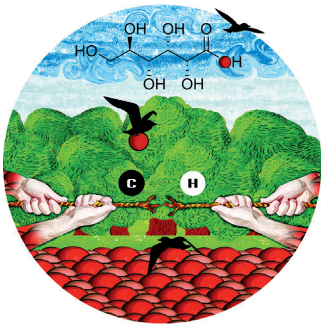
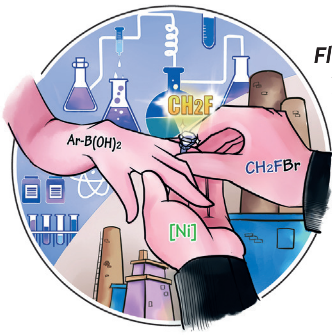
Boron-containing 1,2,4-amphoteric molecules …



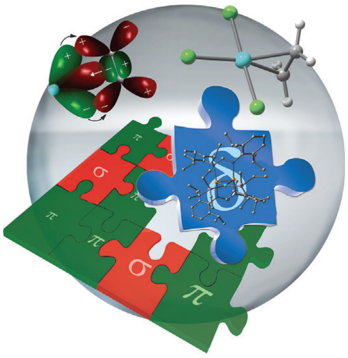
… for generating borylated heterocycles with C–C bonds in uncommon positions are described by A. K. Yudin et al. in their Communication on page 9038 ff. If the boron-containing heterocycles are likened to flowers, the newly developed molecules would be the sprouts of this new approach, and the growth of the shoots through the soil the production of 1,4-dicarbonylboronate intermediates upon photoredox-mediated “germination”. The intermediates undergo condensation reactions with a range of nucleophiles, blossoming into heterocycles of medicinal significance.



Sustainable Chemistry
In their Communication on page 8928 ff., Y. Yang, S. H. Mushrif, and co-workers show that an oxygen atom of an surface lattice of copper oxide activates the formyl C–H bond in glucose.



Fluoromethylation
In their Communication on page 9079 ff., X. Zhang et al. report an efficient and straightforward strategy for the Ni-catalyzed fluoromethylation of aryl boronic acids employing the industrial raw material CH_2FBr as the coupling partner.



δ Complexes
Y.-C. Tsai et al. present compounds in their Communication on page 9106 ff. in which a Mo–Mo pentuple bond acts as a ligand for transition-metal complex fragments. The bonding situation in these δ complexes can be described by the Dewar–Chatt model.

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Author Profile

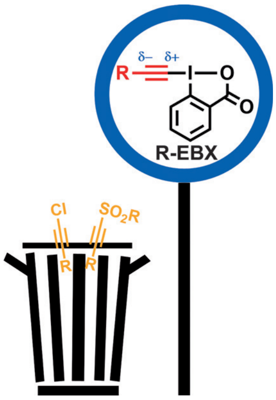
"My "science heroes" are Otto Hahn and Hans Hellmann. My favorite authors are Walter Kempowski and John Updike ..."
This and more about Richard Dronskowski can be found on page 8872.

Books

Highlights

Hypervalent Iodine Reagents

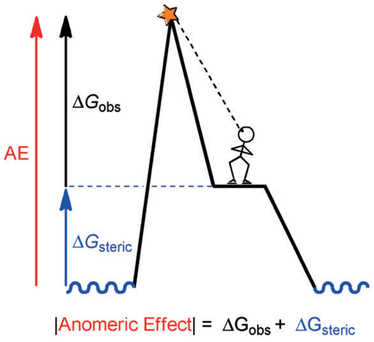
Umpolung of alkynes: The hypervalent iodine reagent EBX (ethynyl benziodoxolone) can be employed for the electrophilic introduction of alkynes. Aside from its unusual reactivity, mild reaction conditions and a high tolerance towards various functional groups are remarkable features of this stable reagent and its reactions.



Essays

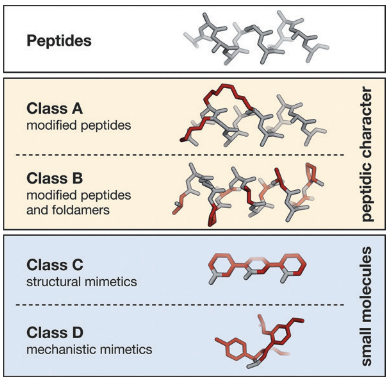
Science Philosophy

Cause and effect: In science, language is often subordinated to empirical data, but words can influence our ability to understand and communicate science. This Essay argues that imprecise language has confounded studies that probe the interactions underlying the anomeric effect and related phenomena.



Reviews

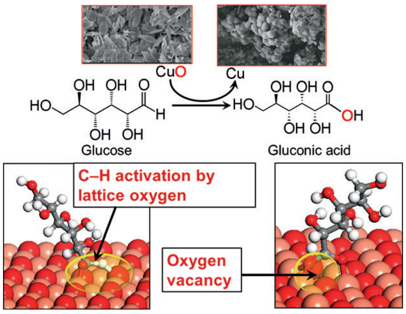
Protein–Protein Interactions



A matter of class: Inhibitors of protein–protein interactions can be obtained by mimicking peptide binding epitopes in their bioactive conformation. For this purpose, several strategies have been evolved to yield molecules that are generally referred to as peptidomimetics. This Review highlights these approaches and introduces a new classification for peptidomimetics that enables a clear assignment of available approaches.

Communications

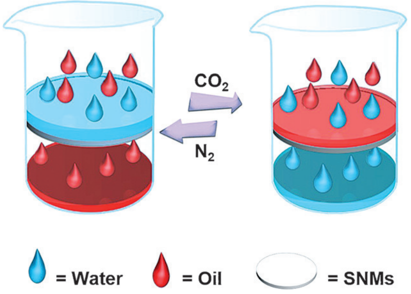
Sustainable Chemistry



The lattice oxygen: An integrated experimental and computational investigation reveals that a surface lattice oxygen of copper oxide activates the formyl C–H bond in glucose. Later this oxygen atom incorporates itself into the glucose molecule to oxidize it to gluconic acid.

Frontispiece

For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.



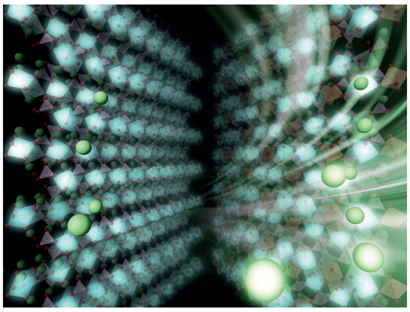
Switchable membrane: A smart electrospun nanostructured polymer membrane (SNM) which is capable of switching oil/water wettability using CO$_2$ as the trigger was developed. Alternate application of CO$_2$ and N$_2$ gas switches the membrane between oil and water permeability (see picture).

Membranes

H. Che, M. Huo, L. Peng, T. Fang, N. Liu, L. Feng, Y. Wei, J. Yuan* **8934 – 8938**

CO$_2$-Responsive Nanofibrous Membranes with Switchable Oil/Water Wettability

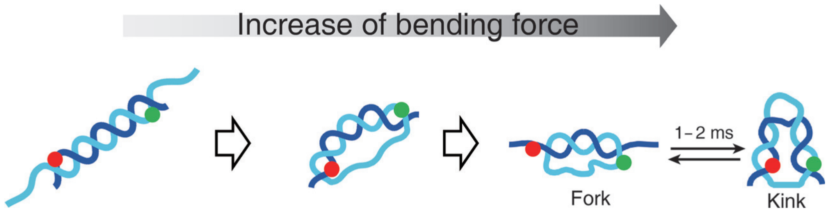
Understanding of intermediate phases in the battery electrode reaction is critical to maximize cell performance. Using a combined analysis of electron, neutron, and X-ray diffraction, a superstructure in the metastable intermediate Li$_{2/3}$FePO$_4$ was determined. The superstructure is stabilized by charge-ordering stripes at Fe sites followed by Li redistribution to optimize the local interactions.



Cathode Materials

S. Nishimura, R. Natsui, A. Yamada* **8939 – 8942**

Superstructure in the Metastable Intermediate-Phase Li$_{2/3}$FePO$_4$ Accelerating the Lithium Battery Cathode Reaction

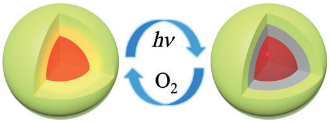


Getting the bends: Strong bending induces two types of short dsDNA deformations, namely a kink in the middle and forks at the ends, as a mechanism of releasing the energy cost of bending (see figure). The two types of deformed dsDNA structures dynamically interconvert on a millisecond timescale. The transition from a fork to a kink is dominated by entropic contributions.

DNA Deformation

C. Kim, O.-C. Lee, J.-Y. Kim, W. Sung, N. K. Lee* **8943 – 8947**

Dynamic Release of Bending Stress in Short dsDNA by Formation of a Kink and Forks



Switchable surface redox chemistry is demonstrated in gold@iron/iron oxide core–shell nanoparticles. The iron shell can be oxidized to iron oxide through ambient oxidation, leading to an enhancement and red-shift of the gold surface plasmon resonance (SPR). The gold SPR in turn can drive reduction of the iron oxide shell under broadband illumination to reversibly blue-shift and significantly dampen gold SPR absorption.

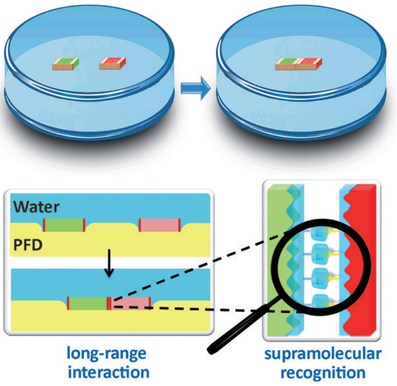
Metal Nanoparticles

Z. Li, J. J. Foley IV, S. Peng, C.-J. Sun, Y. Ren, G. P. Wiederrecht,* S. K. Gray,* Y. Sun* **8948 – 8951**

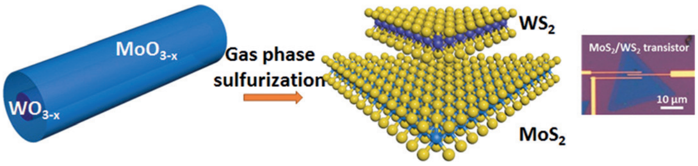
Reversible Modulation of Surface Plasmons in Gold Nanoparticles Enabled by Surface Redox Chemistry

Macroscopic Assembly

Spontaneous locomotion is performed by macroscopic building blocks under the Marangoni effect to reach interactive distance. By increasing the density of the building blocks, the assembly force transforms from a hydrophobic to hydrophilic interaction, which is favorable for introducing hydrophilic coatings with host–guest groups on matched surfaces, consequently realizing the fabrication of stable precise macroscopic supramolecular assemblies. PFD = perfluorodecalin.

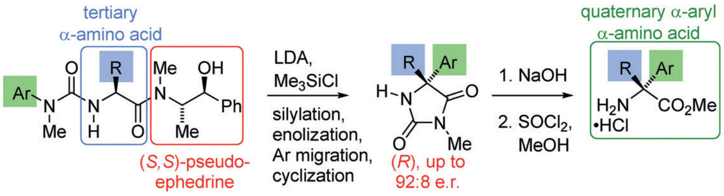


Nanotechnology



2D MoS_2/WS_2 heterostructures were successfully grown by using core–shell WO_{3-x}/MoO_{3-x} nanowires as a precursor in a CVD process. This method opens up a new way to synthesize various functional 2D heterostructures for novel electronic and optoelectronic devices.

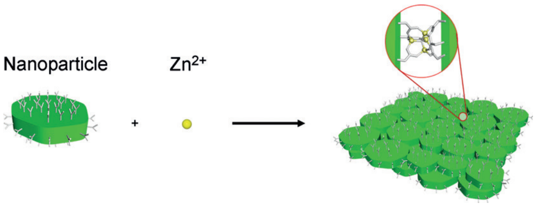
Chiral Auxiliaries



Hydantoins were obtained through the asymmetric α-arylation of α-amino acids by pseudoephedrine-directed tandem rearrangement and cyclization of their silylated N-aryl urea derivatives. The hydantoins could be hydrolyzed to enantioenriched α-arylated quaternary amino acids.

Self-Assembled Materials

Inside Cover

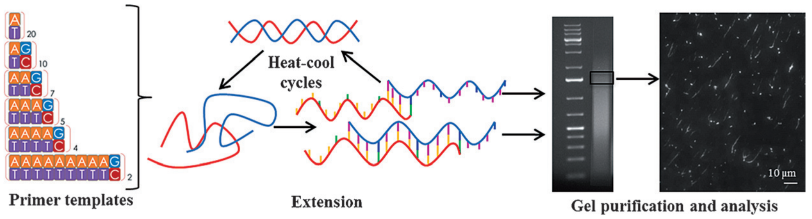


Zinc ions are the "glue": FeS_2 nanoparticles (NPs) spontaneously assemble into sheets because of coordination bridging between Zn^{2+} and carboxylate groups on the NP surface. Conductivity and Hall carrier mobility of the p-type semiconductor films exceed those known for coordination compounds and MOFs. The nanoscale porosity and fast hole transport of assembled sheets leads to high electrocatalytic activity of the NP films.

DNA Nanotechnology

C. J. Whitfield, A. T. Turley, E. M. Tuite, B. A. Connolly, A. R. Pike* ___ **8971 – 8974**

Enzymatic Method for the Synthesis of Long DNA Sequences with Multiple Repeat Units

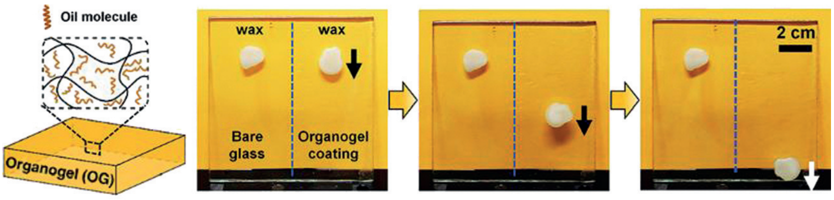


Multiple repeats: A flexible enzymatic route for the synthesis of long DNA segments that contain multiple repeat units of 1–10 bases has been developed. DNA sequences of 500 to 20000 base pairs were readily synthesized and purified and could find applications as functional nanomaterial building blocks.

Organogels

X. Yao, S. Wu, L. Chen, J. Ju, Z. Gu, M. Liu, J. Wang,* L. Jiang ___ **8975 – 8979**

Self-Replenishable Anti-Waxing Organogel Materials

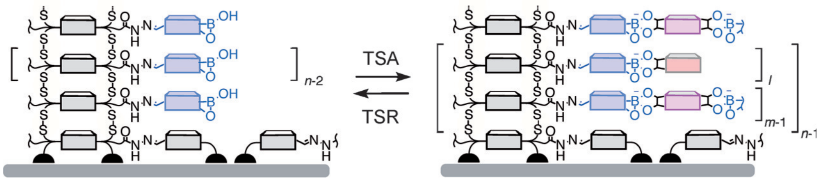


Wax on, wax off: Organogel materials, prepared by swelling a crosslinked poly(dimethylsiloxane) network with low-molar-mass components of crude oil, show ultra-low adhesion to solidified paraffin wax. The self-replenishing organogel shows great potential to prevent wax deposition both in flow and static modes.

Dynamic Covalent Chemistry

K.-D. Zhang, S. Matile* ___ **8980 – 8983**

Complex Functional Systems with Three Different Types of Dynamic Covalent Bonds

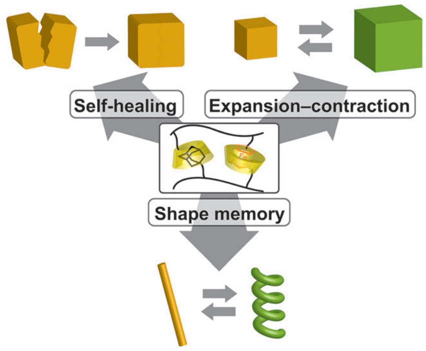


Designer architectures: Disulfide exchange under basic conditions, hydrazone exchange under acidic conditions, and boronic ester exchange at neutral pH values are combined to build multicomponent functional surface architectures using dynamic covalent chemistry. TSA/TSR = templated stack addition/release.

Polymeric Materials

K. Miyamae, M. Nakahata, Y. Takashima, A. Harada* ___ **8984 – 8987**

Self-Healing, Expansion–Contraction, and Shape-Memory Properties of a Preorganized Supramolecular Hydrogel through Host–Guest Interactions



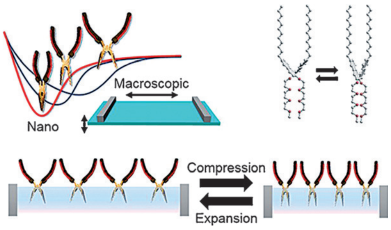
Nonconventional intelligence: Multifunctional supramolecular materials are expected to be the next generation of intelligent soft materials. Supramolecular polymeric materials were created through host–guest interactions (instead of conventional covalent cross-linking) to form two different kinds of host–guest inclusion complexes. The resulting gels displayed the properties of self-healing, expansion–contraction, and shape memory (see picture).

Mechanochemistry

D. Ishikawa, T. Mori, Y. Yonamine, W. Nakanishi,* D. L. Cheung,* J. P. Hill, K. Ariga* ______ **8988 – 8991**

Mechanochemical Tuning of the Binaphthyl Conformation at the Air–Water Interface

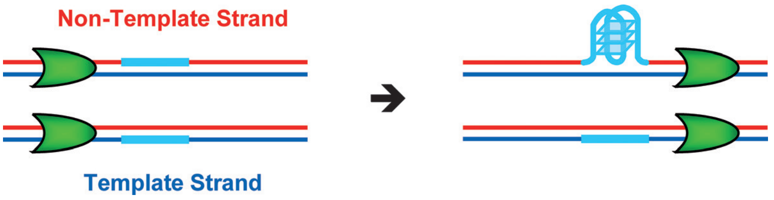
2D interface for mechanochemistry: Mechanical force was used to tune the torsion angle of an amphiphilic binaphthyl molecular pliers at the air–water interface. Dynamic and repeatable control of the structure was achieved.



G-Quadruplexes

J.-q. Liu, S. Xiao, Y.-h. Hao, Z. Tan* ______ **8992 – 8996**

Strand-Biased Formation of G-Quadruplexes in DNA Duplexes Transcribed with T7 RNA Polymerase

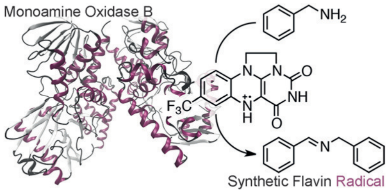


Strand discrimination: During transcription, the different interactions between a T7 RNA polymerase and the two strands of a DNA duplex result in G-quadruplex formation on the non-template strand, but not on the template strand. Structural analysis reveals that the polymerase induces distortion in the DNA duplex both inside and in front of the enzyme.

Enzymes

A. T. Murray, M. J. H. Dowley, F. Pradaux-Caggiano, A. Baldansuren, A. J. Fielding, F. Tuna, C. H. Hendon, A. Walsh, G. C. Lloyd-Jones, M. P. John, D. R. Carbery* ______ **8997 – 9000**

Catalytic Amine Oxidation under Ambient Aerobic Conditions: Mimicry of Monoamine Oxidase B



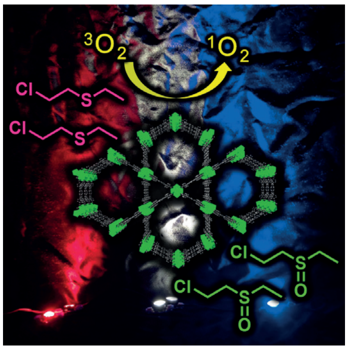
MAO copycat: Mimicry of monoamine oxidase B (MAO B) under aerobic and ambient conditions has been accomplished using a model flavin. Kinetic and EPR studies have offered mechanistic insight, ultimately allowing an appreciation of kinetic similarity to already published data concerning MAO B. A rate-contributing hydrogen-atom transfer from the amine substrate to the flavin acceptor is proposed for both the model system and MAO B.

Chemical Warfare Agents

Y. Liu, A. J. Howarth, J. T. Hupp,* O. K. Farha* ______ **9001 – 9005**

Selective Photooxidation of a Mustard-Gas Simulant Catalyzed by a Porphyrinic Metal–Organic Framework

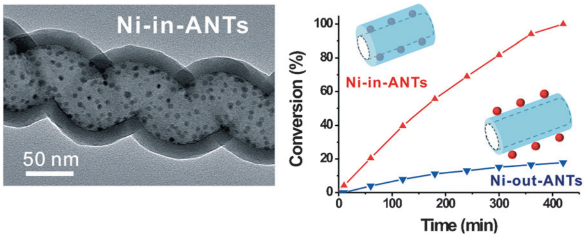
Lights, camera, oxidation! Inexpensive and commercially available LEDs are used to generate singlet oxygen with a MOF catalyst. The singlet oxygen is then used for the selective oxidation of a mustard-gas simulant, 2-chloroethyl ethyl sulfide, to give relatively nontoxic 2-chloroethyl ethyl sulfoxide; this safe, convenient, and effective process proceeds without formation of the toxic sulfone.



Heterogeneous Hydrogenation

Z. Gao, M. Dong, G. Z. Wang, P. Sheng,
Z. W. Wu, H. M. Yang, B. Zhang,
G. F. Wang, J. G. Wang,
Y. Qin* ______ **9006 – 9010**

Multiply Confined Nickel Nanocatalysts Produced by Atomic Layer Deposition for Hydrogenation Reactions

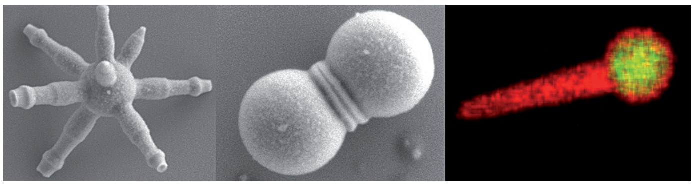


Nanoreactor: A template-assisted atomic layer deposition method was employed to synthesize Ni nanoparticles not only confined in Al_2O_3 nanotubes (ANTs), but also to the cavities of the tube interior wall. The increased metal–support interface and protecting nanotubes lead to greatly improved activity and stability for hydrogenation of cinnamaldehyde and nitrobenzene.

Hierarchical Structures

P. Datskos, D. A. Cullen,
J. Sharma* ______ **9011 – 9015**

Step-by-Step Growth of Complex Oxide Microstructures

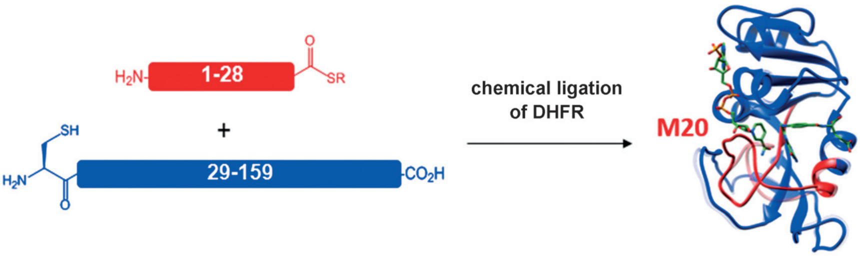


Complex and hybrid oxide structures were grown by exploiting the emulsion-droplet-based SiO_2 deposition. A variety of structures such as corrugated spiky silica structures, a silica ring sandwiched in a particle dimer, and SiO_2–TiO_2 hybrid structures were synthesized with good control of morphology using the same growth strategy.

Protein Dynamics

L. Y. P. Luk, J. J. Ruiz-Pernía, A. S. Adesina,
E. J. Loveridge, I. Tuñón,* V. Moliner,*
R. K. Allemann* ______ **9016 – 9020**

Chemical Ligation and Isotope Labeling to Locate Dynamic Effects during Catalysis by Dihydrofolate Reductase

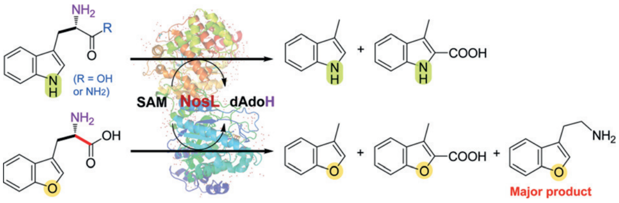


Heavy enzyme: Two dihydrofolate reductase (DHFR) hybrids were prepared; one hybrid contained heavy isotopes (^2H, ^{13}C, ^{15}N) only in the mobile N-terminal segment, whereas in the other hybrid, only the C-terminal segment was isotopically labeled. Kinetic studies showed that isotopic substitution of the N-terminal segment affected only a physical step of catalysis, whereas the enzyme chemistry was affected by protein motions from the C-terminal segment.

Biosynthesis

X. Ji, Y. Li, W. Ding,
Q. Zhang* ______ **9021 – 9024**

Substrate-Tuned Catalysis of the Radical *S*-Adenosyl-L-Methionine Enzyme NosL Involved in Nosiheptide Biosynthesis

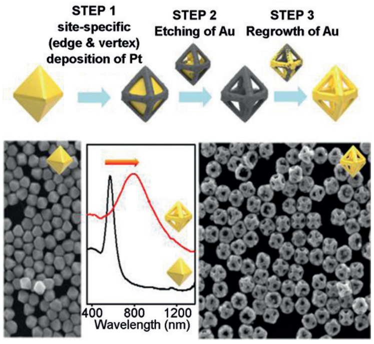


Catalytic promiscuity: NosL is a radical *S*-adenosyl-L-methionine (SAM) enzyme that converts L-Trp to 3-methyl-2-indolic acid, a key intermediate in the biosynthesis of a thiopeptide antibiotic nosiheptide. NosL catalysis is investigated by using a series of Trp analogues as the molecular probes. The results indicate that NosL is transformed to a novel decarboxylase by an unnatural substrate.

Gold Nanostructures

S. Ham, H.-J. Jang, Y. Song,
K. L. Shuford,* S. Park* ____ **9025 – 9028**

Octahedral and Cubic Gold Nanoframes with Platinum Framework

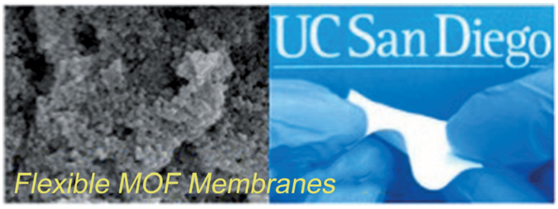


From solid to frame: Octahedral and cubic 3D Au nanoframes are synthesized through site-selective deposition of Pt on edges and vertexes of gold nanoparticles followed by a Au etching/regrowth process. Their high homogeneity allowed detailed characterization of corresponding surface plasmon bands. The synthesis strategy may create unprecedented nanostructures with applications in optical, biomedical, and catalytic fields.

Mixed-Matrix Membranes

M. S. Denny, Jr.,
S. M. Cohen* ____ **9029 – 9032**

In Situ Modification of Metal–Organic Frameworks in Mixed-Matrix Membranes

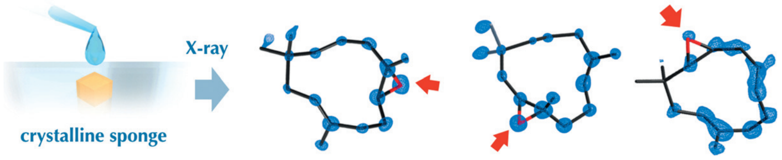


Triple M: Mixed-matrix membranes (MMMs) were obtained from a wide range of metal–organic frameworks. The membranes are flexible, easily handled, and contain highly crystalline MOFs, with large surface areas that remain amenable to chemical modification by postsynthetic methods.

Host–Guest Systems

N. Zigon, M. Hoshino, S. Yoshioka,
Y. Inokuma, M. Fujita* ____ **9033 – 9037**

Where is the Oxygen? Structural Analysis of α-Humulene Oxidation Products by the Crystalline Sponge Method



Soaking it all up: α-Humulene, a cyclic sesquiterpene, was converted into its oxidized subproducts using different reaction conditions. The product structures were obtained by the crystalline sponge method, and their regio- and stereochemistry, absolute configuration, and stable conformations were determined for samples on a 5–50 μg scale. Atom colors: O = red; C = black. F_o electron density map = blue.

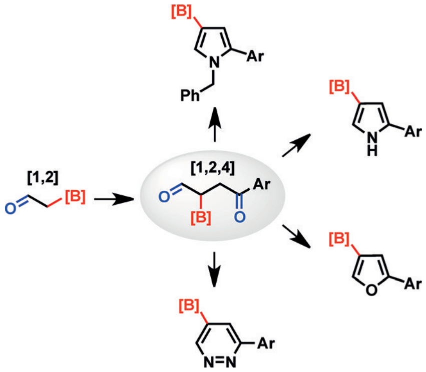
Borylated Heterocycles

P. Trinchera, V. B. Corless,
A. K. Yudin* ____ **9038 – 9041**

Synthesis of Previously Inaccessible Borylated Heterocycle Motifs Using Novel Boron-Containing Amphoteric Molecules

Front Cover

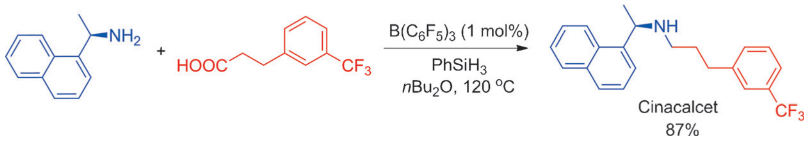
The α-alkylation of α-MIDA boryl aldehyde provides a range of boron-containing 1,4-dicarbonyl compounds. The participation of these 1,2,4-amphoteric molecules in double-condensation reactions with different nucleophiles leads to the formation of borylated heterocycles featuring uncommon substitution patterns ([B] = *N*-methyliminodiacetyl boronate).



Synthetic Methods

M.-C. Fu, R. Shang,* W.-M. Cheng, Y. Fu* **9042 – 9046**

Boron-Catalyzed N-Alkylation of Amines using Carboxylic Acids

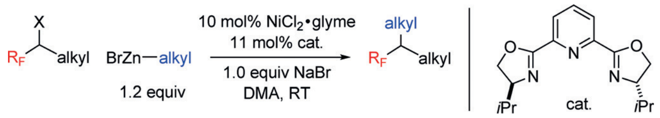


Perfluorinated triphenyl borane catalyzes the straightforward alkylation of amines with carboxylic acids in the presence of a silane as the reducing agent. Both primary and secondary amines can be alkylated with good selectivity and good functional-group compatibility. Three drug molecules, Butenafine, Cinacalcet, and Piribedil, were synthesized in a one-pot manner without using any metal catalysts.

Homogeneous Catalysis

Y. Liang, G. C. Fu* **9047 – 9051**

Nickel-Catalyzed Alkyl–Alkyl Cross-Couplings of Fluorinated Secondary Electrophiles: A General Approach to the Synthesis of Compounds having a Perfluoroalkyl Substituent

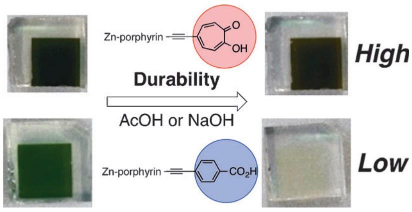


A new pairing: A mild, convenient, and versatile method for the synthesis of compounds bearing a perfluoroalkyl group on a tertiary carbon atom is described. The title reaction results in the coupling of a wide range of fluorinated alkyl halides with alkylzinc reagents at room temperature. A broad array of functional groups are compatible with the reaction conditions, and preliminary mechanistic studies are discussed. DMA = N,N-dimethylacetamide.

Photovoltaic Devices

T. Higashino, Y. Fujimori, K. Sugiura, Y. Tsuji, S. Ito, H. Imahori* **9052 – 9056**

Tropolone as a High-Performance Robust Anchoring Group for Dye-Sensitized Solar Cells

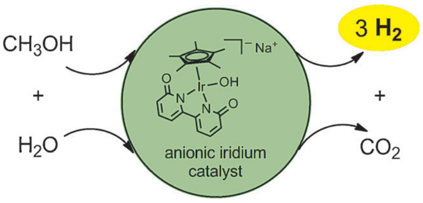


Hang in there! Tropolone was found to be a promising anchoring group for dye-sensitized solar cells (DSSCs). It was used to attach a porphyrin to a TiO_2 surface and would also be suitable for anchoring other types of dyes. A DSSC based on a porphyrin with a tropolone moiety exhibited comparable power-conversion efficiency and superior durability to those of a DSSC based on a reference porphyrin with a carboxylic group (see picture).

Hydrogen Generation

K. Fujita,* R. Kawahara, T. Aikawa, R. Yamaguchi* **9057 – 9060**

Hydrogen Production from a Methanol–Water Solution Catalyzed by an Anionic Iridium Complex Bearing a Functional Bipyridonate Ligand under Weakly Basic Conditions

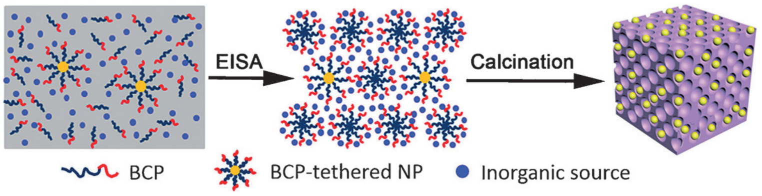


Mild conditions: A new system for hydrogen production from a methanol–water solution under mild conditions (weakly basic solution below 100 °C) has been developed using an anionic iridium catalyst bearing a functional bipyridonate ligand. Long-term continuous hydrogen production has also been achieved.

Mesoporous Catalysts

B. Liu, C.-H. Kuo, J. Chen, Z. Luo, S. Thanneeru, W. Li, W. Song, S. Biswas, S. L. Suib,* J. He* ______ **9061 – 9065**

Ligand-Assisted Co-Assembly Approach toward Mesoporous Hybrid Catalysts of Transition-Metal Oxides and Noble Metals: Photochemical Water Splitting

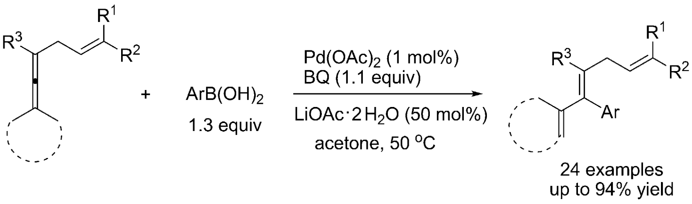


A bottom-up synthetic approach to mesoporous transition-metal-oxide/noble-metal hybrid catalysts involves the ligand-assisted self-assembly of amphiphilic block-copolymer (BCP) micelles and polymer-tethered noble-metal nanoparticles (NPs). The hybrid catalysts were shown to mediate the photochemical oxidation of water. EISA = evaporation-induced self-assembly.

Allene Arylation

C. Zhu, B. Yang, T. Jiang, J.-E. Bäckvall* ______ **9066 – 9069**

Olefin-Directed Palladium-Catalyzed Regio- and Stereoselective Oxidative Arylation of Allenes

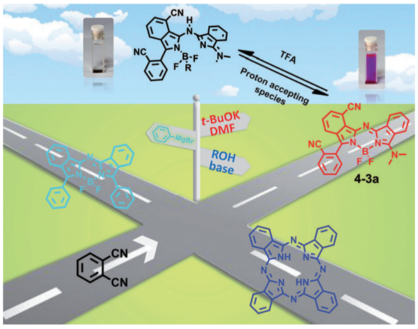


The allylic C=C bond is an indispensable element in the title reaction (see scheme). A series of functionalized allenes, including 2,3- and 3,4-dienoates and 3,4-dienol derivatives, underwent this transformation. Mechanistic studies indicate that cleavage of the allenylic C–H bond is the rate-determining step.

Aza-BODIPY Dyes

W. Zheng, B.-B. Wang, C.-H. Li,* J.-X. Zhang, C.-Z. Wan, J.-H. Huang, J. Liu, Z. Shen,* X.-Z. You* ______ **9070 – 9074**

Asymmetric Donor–π-Acceptor-Type Benzo-Fused Aza-BODIPYs: Facile Synthesis and Colorimetric Properties

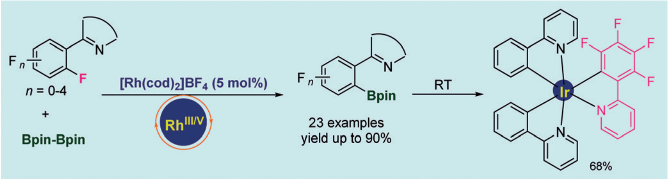


Dyes at the crossroads: By using *t*BuOK/DMF as base to ionize the phthalonitrile, we have developed a facile method to synthesize asymmetric donor–π-acceptor-type benzo-fused aza-BODIPY complexes. The newly prepared aza-BODIPYs exhibit novel colorimetric properties which could be attributed to the fracturing and restoration of the B–N bond.

C–F Activation

W.-H. Guo, Q.-Q. Min, J.-W. Gu, X. Zhang* ______ **9075 – 9078**

Rhodium-Catalyzed *ortho*-Selective C–F Bond Borylation of Polyfluoroarenes with Bpin–Bpin



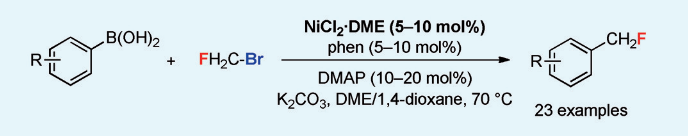
$Rh^{III/V}$ for borylation: The significant features of the title reaction are the simple catalytic system, the broad substrate scope, and the efficient synthesis of photoelectronic materials. A $Rh^{III/V}$ catalytic cycle is proposed for the reaction, which involves a rhodium(III) hydride complex as a key intermediate.

Fluoromethylation

L. An, Y.-L. Xiao, Q.-Q. Min, X. Zhang* ______ **9079 – 9083**

Facile Access to Fluoromethylated Arenes by Nickel-Catalyzed Cross-Coupling between Arylboronic Acids and Fluoromethyl Bromide

Inside Back Cover

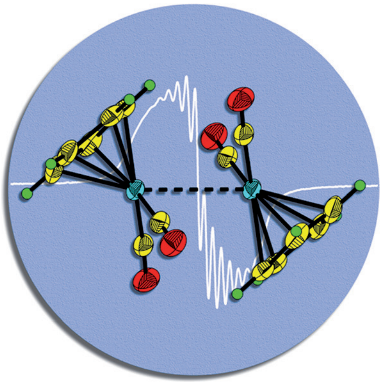


Efficient and straightforward: The title reaction is characterized by synthetic simplicity, employing a low-cost nickel catalyst and the industrial raw material CH_2FBr as a coupling partner. It enables the late-stage fluoromethylation of biologically relevant molecules. Preliminary mechanistic studies show that a single-electron-transfer pathway is involved in the catalytic cycle. DMAP = 4-dimethylaminopyridine, DME = 1,2-dimethoxyethane, phen = 1,10-phenanthroline.

Metal Carbonyl Chemistry

X. Zheng, X. Wang, Z. Zhang, Y. Sui, X. Wang,* P. P. Power* ____ **9084 – 9087**

Access to Stable Metalloradical Cations with Unsupported and Isomeric Metal–Metal Hemi-Bonds



Metal–metal interactions: Three metalloradical cations are stabilized with weakly coordinating polyfluoroaluminate anions in the solid state, featuring supported, unsupported (see picture) and isomeric cobalt–cobalt hemi-bonds (bond order about 0.5). The first examples of isolable unsupported metal–metal hemi-bonds are reported, suggesting that other similar metalloradical species are accessible too.

Hydrosilylation

Z. D. Miller, R. Dorel, J. Montgomery* ______ **9088 – 9091**

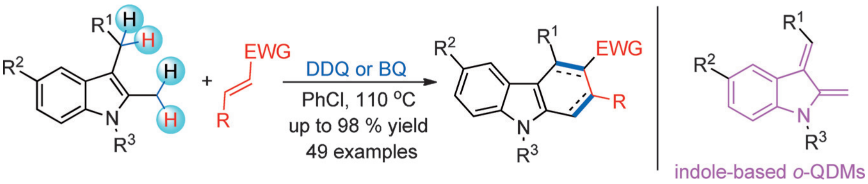
Regiodivergent and Stereoselective Hydrosilylation of 1,3-Disubstituted Allenes

Silanes with a choice: The hydrosilylation of 1,3-disubstituted allenes, which have presented a notorious challenge for regioselective additions, can now be accomplished with outstanding levels of regio- and stereocontrol. By altering the metal catalyst and ligand structure, access to trisubstituted *Z* alkenylsilanes or *trans* allylsilanes is provided in a simple catalytic operation.

Cycloaddition

L. Zhou, B. Xu, J. Zhang* ____ **9092 – 9096**

Metal-Free Dehydrogenative Diels–Alder Reactions of 2-Methyl-3-Alkylindoles with Dienophiles: Rapid Access to Tetrahydrocarbazoles, Carbazoles, and Heteroacenes

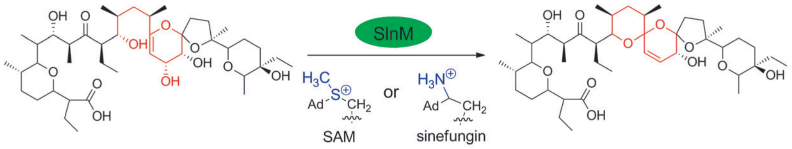


Setting a trap: Described is a strategy for in situ generation of indole-based *ortho*-quinodimethanes (*o*QDMs) from the title indoles through either a DDQ- or BQ-mediated dehydrogenative process. These *o*QDMs are trapped by electron-deficient olefins, thus providing facile access to tetrahydrocarbazoles, carbazoles, and hetereoacenes. BQ = benzoquinone, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Biosynthesis

C. Jiang, Z. Qi, Q. Kang, J. Liu, M. Jiang, L. Bai* ——— 9097 – 9100

Formation of the $\Delta^{18,19}$ Double Bond and Bis(spiroacetal) in Salinomycin Is Atypically Cataly'zed by SlnM, a Methyltransferase-like Enzyme



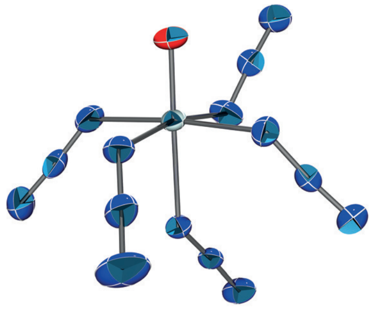
Think positive: By using *S*-adenosylmethionine (SAM) or sinefungin (a methylation inhibitor) as a cofactor, SlnM, a methyltransferase homologue, was shown to catalyze the spirocyclization-coupled dehydration of C19 in salinomycin biosynthesis. SAM, or more specifically its positive charge, has been considered to be essential in the enzymatic conversion.

Vanadium Oxoazides

R. Haiges,* M. Vasiliu, D. A. Dixon, K. O. Christe ——— 9101 – 9105

The Vanadium(V) Oxoazides $[VO(N_3)_3]$, $[(bipy)VO(N_3)_3]$, and $[VO(N_3)_5]^{2-}$

Handle with care: Vanadium(V) oxoazides were prepared and characterized for the first time. $[VO(N_3)_3]$ was obtained from $[VOF_3]$ and Me_3SiN_3 as a very friction- and impact-sensitive solid. The reaction of $[VO(N_3)_3]$ with 2,2′-bipyridine and $[PPh_4]N_3$ afforded $[(bipy)VO(N_3)_3]$ and $[PPh_4]_2[[VO(N_3)_5]$, respectively, which were characterized by single-crystal X-ray structure determination.



$[VO(N_3)_5]^{2-}$

DOI: 10.1002/anie.201583114

Flashback: 50 Years Ago . . .

The field of organic semiconducors is a hot topic today, and 50 years ago the area was already attracting some interest as scientists were keen to know whether organic compounds showed similar behavior to the better known inorganic semiconductors. In a Review, Hans Meier discussed the photoconduction properties of organic dyes, including n- and p-type conductivity. Polythiophenes, cyanine dyes, and phthalocyanine derivatives were among the compounds described.

Carrying out experiments in liquid hydrogen fluoride is certainly not for the faint hearted, however studies on the reaction of liquid hydrogen fluoride (which is a stronger acid than its aqueous counterpart) with nitrous acid and its derivatives were indeed carried out, as outlined in a Review by Fritz Seel. The products of these reactions contained nitrosyl fluoride solvated by hydrogen fluoride, and are valuable reagents in fluorine chemistry.

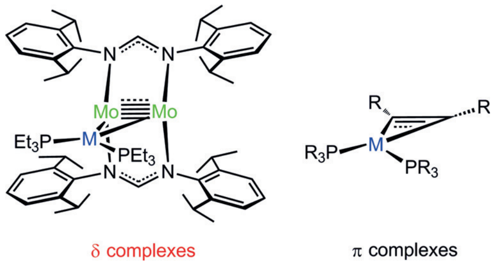
André S. Dreiding reported on a rearrangement of *ar*-tetralols. When 1,2,3,4,6,9-hexahydro-6-oxo-9-methylnaphthalene was heated with sulfuric acid, 8-methyl-5-tetralol was the major product, and when mineral acids were used then 5-methyl-7-tetralol was the major product. However, with 70 % perchloric acid, 7-methyl-5-tetralol was the sole product. The differences were ascribed to the reactions being either under kinetic or thermodynamic control. Dreiding was the founder of the famous Bürgenstock Conference, which celebrated its 50th anniversary this year (for more details see *Angew. Chem. Int. Ed.* **2015**, *54*, 5014).

Ekkehart Winterfeldt published a Communication on the stereochemistry of the addition reactions to acetylenic triple bonds. Mechanistic studies showed that the *cis* adducts are produced by a cyclic electron shift, and contradicted previous claims that compounds with easily abstractable hydrogen atoms always undergo *trans* addition reactions. Winterfeldt's Obituary can be read at *Angew. Chem. Int. Ed.* **2015**, *54*, 35.

Read more in Issue 8/1965.

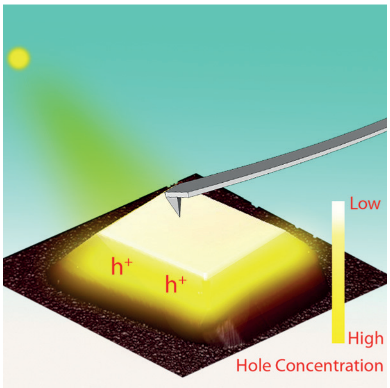
Metals as Ligands

Back Cover



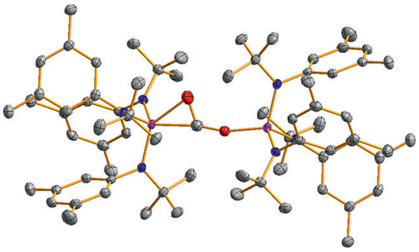
Akin to alkenes and alkynes, which form metal π complexes upon coordinating to metal fragments, the Mo–Mo quintuple-bonded amidinate serves as a δ type of ligand binding Group 10 metal elements to give rise to the formation of the first examples of δ complexes.

Photocatalysis



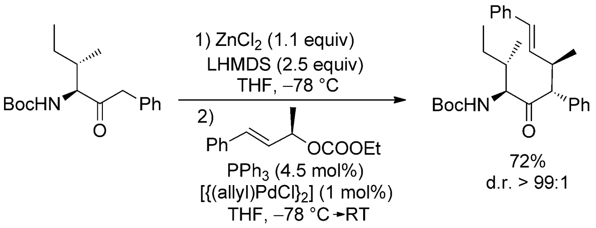
Spatially resolved surface photovoltage spectroscopy (SRSPS) was employed to obtain first direct evidence of highly anisotropic photogenerated charge separations on different facets of a single BiVO$_4$ photocatalyst. The results provide guidance to optimizing the performance of photocatalysts and solar cells.

Dimetalloxycarbene Complexes



Between a rock and a hard place: A structurally characterized dimetalloxycarbene complex, which is stabilized by coordination of the carbenoid carbon atom on two metal centers (see picture: C gray, N blue, O red, Ti magenta), reacts with CO$_2$ to form an oxalate complex. DFT calculations show that nucleophilic attack of a free carbene species occurs on CO$_2$.

Allylic Alkylation



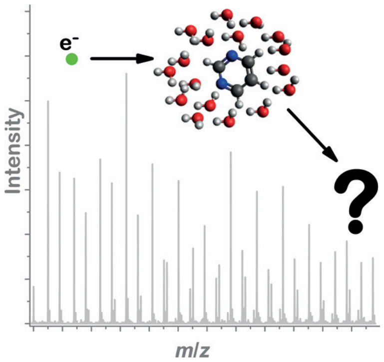
Chiral α-amino ketones are excellent nucleophiles for highly stereoselective palladium-catalyzed allylic alkylations with chiral as well as achiral allylic substrates. The substituted amino ketone products are interesting building blocks for synthetic applications.

Mass Spectrometry

M. Neustetter, J. Aysina, F. F. da Silva,* S. Denifl* ______ **9124 – 9126**

The Effect of Solvation on Electron Attachment to Pure and Hydrated Pyrimidine Clusters

Low-energy electrons lead to efficient decomposition of single biomolecules in the gas phase. The situation radically changes when the molecules are solvated. Pure and hydrated clusters of pyrimidine were formed and exposed to low-energy electrons. The monomer anion of pyrimidine can be stabilized only in the case of pure pyrimidine clusters and when the anion is first electronically excited.



Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Angewandte Corrigendum

Composite Aromatic Boxes for Enzymatic Transformations of Quaternary Ammonium Substrates

G. N. Nagy,* L. Marton, A. Contet, O. Ozohanics, L.-M. Ardelean, Á. Révész, K. Vékey, F. D. Irimie, H. Vial, R. Cerdan, B. G. Vértessy* ______ **13471–13476**

Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201408246

The authors of this Communication would like to add the following two sentences to the acknowledgement:

"We would like to thank Professor Ferenc Erdődi and Bálint Bécsi (University of Debrecen, Department of Medical Chemistry, Faculty of Medicine, Hungary) for the possibility of ITC measurements. The research work has been accomplished in the framework of the 'BME R+D+I project', supported by the grant TÁMOP 4.2.1/B-09/1/KMR-2010-0002."