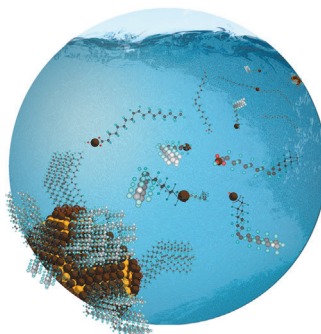




... densely packed with valerates (pictured as juggling balls) are very stable and indicate the unique possibility of hydrophobic clustering inside a cavity, as reported by A. Müller and co-workers in their Communication on page 6634 ff. The clusters remain intact at temperatures of up to nearly the boiling point of water (©jokatoons/bildkistl, Fotolia.com).

Quantum Dots

C. Giansante and co-workers show in their Communication on page 6628 ff. that PbS quantum dots exist in solution as equilibrium mixtures with their (metal-)organic ligand and inorganic core components.

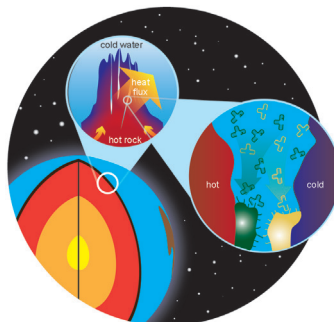


Solar Cells

In their Communication on page 6708 ff., D. Deng, W.-H. Zhang et al. incorporate single Co active sites within graphene to obtain a material with superior activity and stability when used as a counter electrode for I^-/I_3^- interconversion.

Sequence Selection

C. B. Mast and co-workers show in their Communication on page 6676 ff. how a ubiquitous heat flux across a pore separates different DNA sequences with single-base resolution, an essential prebiotic process for the emergence of life.



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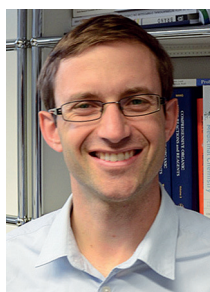
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Spotlight on Angewandte's Sister Journals

6579 – 6582



*"My biggest motivation is to see young students become independent researchers.
My best investment was to wait one year for a good PhD student to join my group ..."*
This and more about Jérôme Waser can be found on page 6583.

Service

Author Profile

Jérôme Waser _____ 6583



D. Trauner



T. Gaich



O. Vázquez



S. Kaskel

News

Otto Bayer Award:
D. Trauner _____ 6584

Bayer Early Excellence in Science Award:
T. Gaich _____ 6584

Cottrell–Fulbright Award:
O. Vázquez _____ 6584

JSPS Prize:
S. Kaskel _____ 6584

Obituary



Robert Corriu, professor emeritus at the Université de Montpellier, passed away at the age of 82 on February 13, 2016. Corriu made many important contributions in the area of silicon chemistry, including hypervalent silicon and transition-metal–silane complexes. He also extended his research to silicon-based (nano)materials such as hybrid organic/inorganic materials and mesoporous silicas.

Robert Corriu (1934–2016)

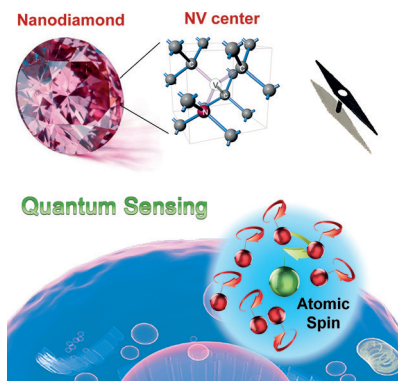
B. Chaudret,* O. Eisenstein _____ 6585

Minireviews

Diamond Quantum Devices

Y. Wu,* F. Jelezko,* M. B. Plenio,*
T. Weil* ————— 6586 – 6598

Diamond Quantum Devices in Biology



Center of attention: Quantum sensors based on the spin-dependent photoluminescence of nitrogen-vacancy (NV) centers in diamond offer imaging with atomic resolution under ambient conditions, which might evolve as a revolutionary technique for the understanding of biomolecules in their native environment. The recent development of this technique, its potential, and challenges are critically discussed.

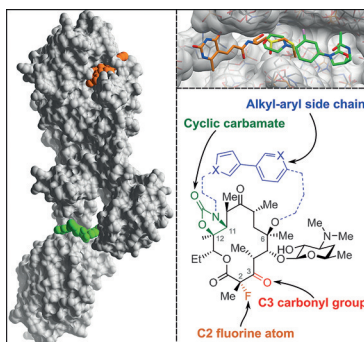
Reviews

Medicinal Chemistry



M. F. Chellat, L. Raguž,
R. Riedl* ————— 6600 – 6626

Targeting Antibiotic Resistance



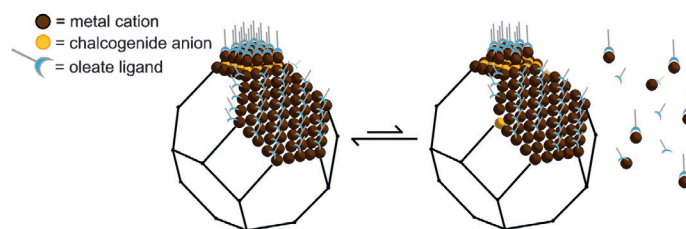
No action today, no cure tomorrow: The development and spread of antibiotic resistance is a global threat to public health. After decades of declining interest in the development of new therapies against infections caused by pathogenic bacteria, a revitalization of antibiotic research has recently taken place. Structure-based and mechanism-based approaches, as well as interventions at the genetic level, hold great promise for conquering antibiotic resistance.

Communications

Quantum Dots

R. Grisorio, D. Debellis, G. P. Suranna,
G. Gigli, C. Giansante* — 6628 – 6633

The Dynamic Organic/Inorganic Interface of Colloidal PbS Quantum Dots



Colloidal quantum dots adapt their composition to their surroundings, existing in the solution phase as equilibrium mixtures with their (metal-)organic ligand and inorganic core components. The inher-

ently dynamic organic/inorganic interface of colloidal quantum dots may open novel possibilities towards improved synthetic procedures and effective surface-chemistry strategies.

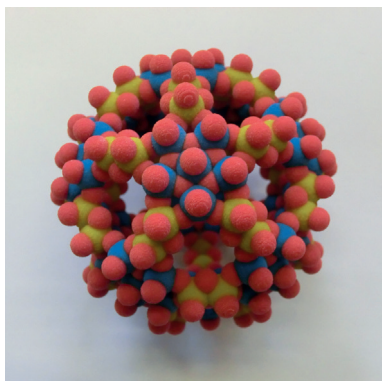
Frontispiece

For the USA and Canada:

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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.



United we stand: A water-soluble metal-oxide nanocapsule entraps 24 valerates to form a densely packed aggregate that is stabilized by hydrophobic interactions in a manner reminiscent of hydrophobic clustering in globular proteins.

Nanocapsules

S. Garai, H. Bögge, A. Merca, O. A. Petina, A. Grego, P. Gouzerh, E. T. K. Haupt, I. A. Weinstock, A. Müller* — **6634–6637**

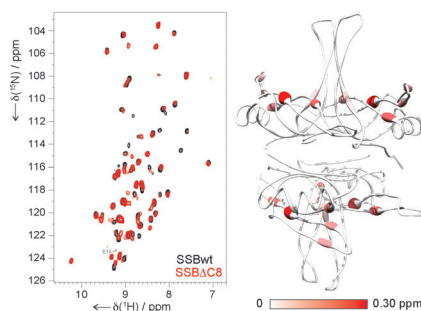
Densely Packed Hydrophobic Clustering: Encapsulated Valerates Form a High-Temperature-Stable $\{\text{Mo}_{132}\}$ Capsule System



Front Cover



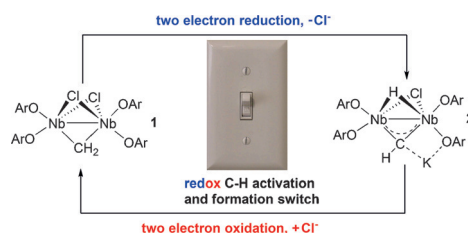
In a spin: A solid-state NMR approach based on high magnetic fields, fast magic-angle spinning, and deuteration was used to provide chemical-shift and relaxation mapping for characterizing the transient association between two regions in a 80 kDa protein assembly, the homotrimeric ssDNA-binding protein (SSB). Comparison of the wildtype (wt) and the truncated mutant SSB Δ Ct led to direct verification of a mechanism of regulation of *E. coli* DNA metabolism.



Protein Structure

H. R. W. Dannatt, M. Felletti, S. Jehle, Y. Wang, L. Emsley, N. E. Dixon, A. Lesage, G. Pintacuda* — **6638–6641**

Weak and Transient Protein Interactions Determined by Solid-State NMR



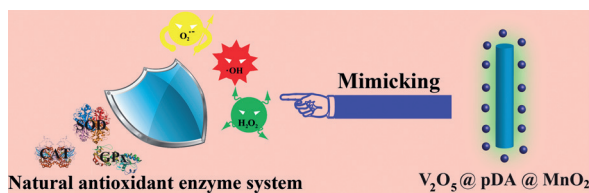
Redox switch: Reduction of the niobium methylidene **1** with KC_8 results in formation of the first niobium methylidyne **2** through binuclear α -hydrogen elimination (see scheme). Oxidation of **2** with ClCPh_3 reforms **1** by virtue of a hydride migration.

When **1** is prepared from $[(\text{Ar}'\text{O})_2\text{Nb}(\text{CH}_3)_2\text{Cl}]$, isotopic labeling studies suggest a radical mechanism, and a binuclear α -hydrogen abstraction being the most likely operative pathway.

Niobium Methylidyne

K. Searles, K. T. Smith, T. Kurogi, C.-H. Chen, P. J. Carroll, D. J. Mindiola* — **6642–6645**

Formation and Redox Interconversion of Niobium Methylidene and Methylidyne Complexes



Artificial enzyme complexes: A multi-nanozyme cooperative platform was constructed to mimic an intracellular antioxidant enzyme-based defense system and

protect cells against oxidative stress (see picture). This development holds great promise for potential applications in cancer and inflammation therapy.

Medicinal Chemistry

Y. Huang, Z. Liu,* C. Liu, E. Ju, Y. Zhang, J. Ren,* X. Qu* — **6646–6650**

Self-Assembly of Multi-nanozymes to Mimic an Intracellular Antioxidant Defense System

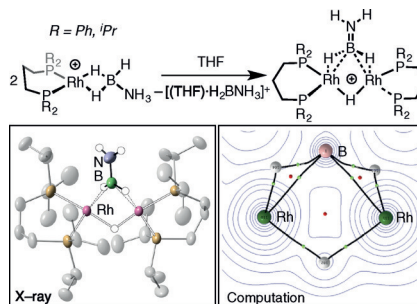


Amine–Borane Dehydropolymerization

A. Kumar, N. A. Beattie, S. D. Pike,
S. A. Macgregor,*
A. S. Weller* — 6651 – 6656



The Simplest Amino-borane $\text{H}_2\text{B}=\text{NH}_2$
Trapped on a Rhodium Dimer: Pre-
Catalysts for Amine–Borane
Dehydropolymerization



Bridges of boron: Mechanistic investigations show that rhodium dimers bridged by amino-borane can form by a boronium-mediated route starting from amine–borane. These types of complexes are pre-catalysts for amine–borane dehydropolymerization, suggesting a possible role for bimetallic motifs in catalysis.

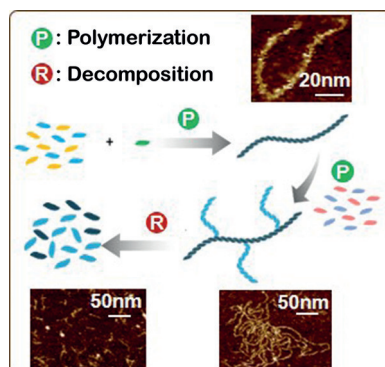


Self-Assembly

N. Chen, X. Shi, Y. Wang* — 6657 – 6661



Molecularly Regulated Reversible DNA
Polymerization



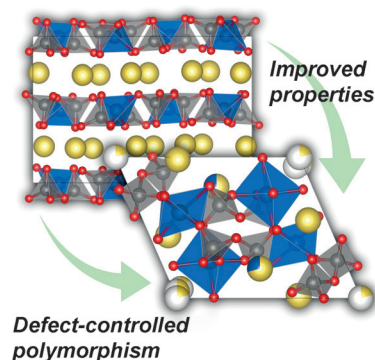
Reversible DNA polymerization: Linear and branched DNA polymers were synthesized and decomposed using molecular triggers under physiological conditions (see picture). The polymerization mechanism is based on the well-known hybridization chain reaction.

Polymorphism

H. Kim, C. S. Park, J. W. Choi,*
Y. Jung* — 6662 – 6666



Defect-Controlled Formation of Triclinic
 $\text{Na}_2\text{CoP}_2\text{O}_7$ for 4 V Sodium-Ion Batteries



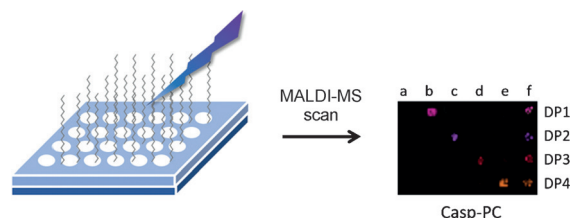
Simple defects such as sodium deficiencies can induce the selective synthesis of triclinic $\text{Na}_2\text{CoP}_2\text{O}_7$, providing an increase in energy density of more than 40% compared to the stoichiometric polymorph that is preferentially formed under the commonly used synthesis conditions. Computational and experimental studies provide insight into the influence of the defects on phase stability.

High-Throughput Screening

J. Hu, F. Liu, H. Ju* — 6667 – 6670

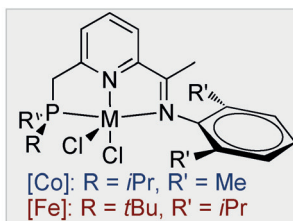
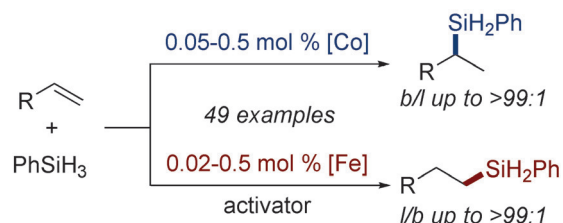


MALDI-MS Patterning of Caspase
Activities and Its Application in the
Assessment of Drug Resistance



Clearly visible: A MALDI-MS patterning strategy for the convenient visual presentation of multiple enzyme activities with an easy-to-prepare chip is proposed. The

activities of various caspases and the development of drug resistance could thus be visualized.



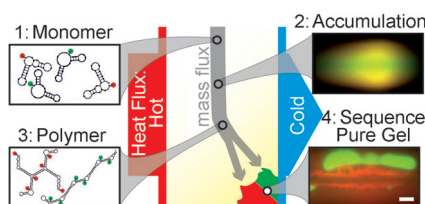
Markovnikov Hydrosilylation

X. Du, Y. Zhang, D. Peng,
Z. Huang* 6671–6675

Base-Metal-Catalyzed Regiodivergent
Alkene Hydrosilylations

Regiodivergent alkene hydrosilylation has been accomplished with high efficiency using a newly developed set of complementary base metal catalyst systems. An inversion of regioselectivity (linear/

branched) from >99:1 to <1:99 is obtained when the iron version of the catalyst is exchanged for a cobalt-containing analogue.



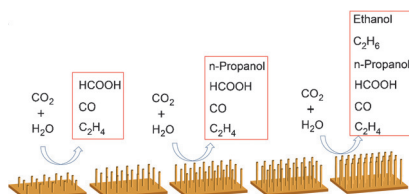
Strand and deliver: The non-equilibrium condition of a moderate heat flow across a water-filled chamber separates and gels DNA strands with single-base resolution. A dilute mix of DNA with two slightly different gel-forming sequences separates into sequence-pure hydrogels under constant physiological solvent conditions. This process points towards new possibilities for non-equilibrium origins of life.

DNA Hydrogels

M. Morasch, D. Braun,
C. B. Mast* 6676–6679

Heat-Flow-Driven Oligonucleotide
Gelation Separates Single-Base
Differences

Back Cover

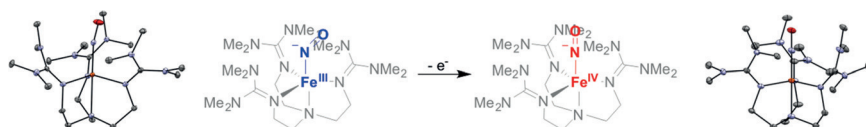


Catalytic activity: A Cu nanowire array for CO₂ reduction was developed. The length and density of the Cu nanowire array could be altered by a simple electroetching method. With varying length and density of the nanowire the chemical selectivity for CO₂ reduction could be systematically tuned. The results provide experimental evidence for a nanostructure-dependent catalytic activity.

Heterogeneous Catalysis

M. Ma, K. Djanashvili,
W. A. Smith* 6680–6684

Controllable Hydrocarbon Formation
from the Electrochemical Reduction of
CO₂ over Cu Nanowire Arrays



One-electron oxidation of the high-spin ferrous nitrosyl complex [Fe(TMGTren)-(NO)]²⁺ yields a rare high-spin (*S* = 1) ferric NO adduct {[FeNO]⁶⁺}. Spectroscopic investigations and DFT calculations indicate that this species has an

Fe^{IV}-NO⁻ electronic structure. This finding demonstrates that high-spin non-heme iron nitrosyl complexes have fundamentally different redox behavior compared to corresponding low-spin heme systems.

Ferric NO Complexes

A. L. Speelman, B. Zhang, C. Krebs,
N. Lehnert* 6685–6688

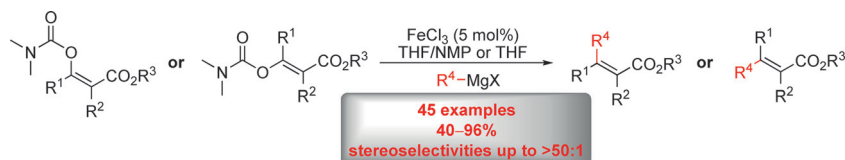
Structural and Spectroscopic
Characterization of a High-Spin {FeNO}⁶⁺
Complex with an Iron(IV)-NO⁻ Electronic
Structure

Cross-Coupling

A. C. P. Rivera, R. Still,
D. E. Frantz* — 6689 – 6693



Iron-Catalyzed Stereoselective Cross-Coupling Reactions of Stereodefined Enol Carbamates with Grignard Reagents



Ironing out olefin synthesis: A practical and highly stereoselective iron-catalyzed cross-coupling reaction between stereo-defined enol carbamates and alkyl

Grignard reagents yields tri- and tetra-substituted acrylates. A facile method for the stereoselective generation of these enol carbamates is also reported.

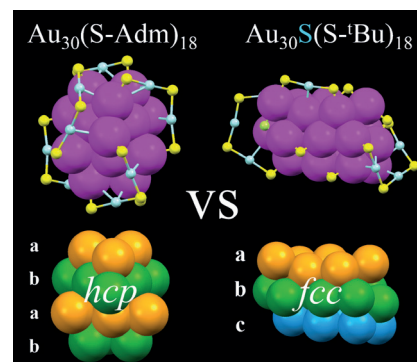
Nanostructures

T. Higaki, C. Liu, C. Zeng, R. Jin, Y. Chen,
N. L. Rosi, R. Jin* — 6694 – 6697



Controlling the Atomic Structure of Au₃₀ Nanoclusters by a Ligand-Based Strategy

In control: Structural control of an Au₃₀ nanocluster is realized through a strategy based on the use of the 1-adamantane-thiol ligand to stabilize the metal core. The newly obtained Au₃₀(S-Adm)₁₈ nanocluster comprises a hexagonal-close-packed kernel protected by six dimeric Au₂(SR)₃ motifs. This structure is different from a previously reported Au₃₀S(S-^tBu)₁₈ cluster that comprises a face-centered-cubic kernel.



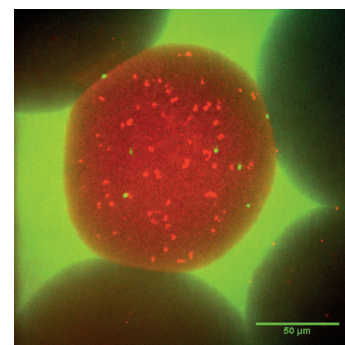
Droplet Microfluidics

A. Rakszewska, R. J. Stolper, A. B. Kolasa,
A. Piruska, W. T. S. Huck* — 6698 – 6701



Quantitative Single-Cell mRNA Analysis in Hydrogel Beads

Catch me if you can: Hydrogel beads functionalized with LNA (locked nucleic acid) can serve as a matrix to capture mRNA from lysed single cells. mRNA quantification free of pre-amplification bias is ensured by using padlock probes and rolling circle amplification followed by hybridization with fluorescent probes. The number of transcripts in individual cells is assessed by counting fluorescent dots inside gel beads. Scale bar = 50 μm.



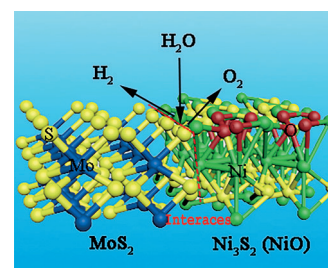
Overall Water Splitting

J. Zhang, T. Wang, D. Pohl, B. Rellinghaus,
R. Dong, S. Liu, X. Zhuang,
X. Feng* — 6702 – 6707

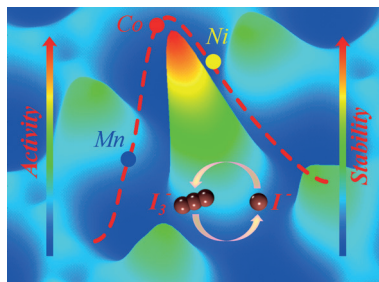


Interface Engineering of MoS₂/Ni₃S₂ Heterostructures for Highly Enhanced Electrochemical Overall-Water-Splitting Activity

Split happens: The preparation of novel MoS₂/Ni₃S₂ heterostructures with abundant interfaces shows that these interfaces synergistically favor the chemisorption of hydrogen and oxygen-containing intermediates, thus leading to highly enhanced water-splitting activity. DFT calculations support these findings.



The incorporation of single cobalt active sites in the basal plane of graphene leads to a composite material with superior activity and stability when used as a counter electrode for the interconversion of the redox couple I^-/I_3^- . DFT calculations revealed the superior properties of CoN_4/GN to be due to the appropriate adsorption energy of iodine on the confined Co sites.



Solar Cells

X. Cui, J. Xiao, Y. Wu, P. Du, R. Si, H. Yang, H. Tian, J. Li, W.-H. Zhang,* D. Deng,* X. Bao ————— **6708–6712**

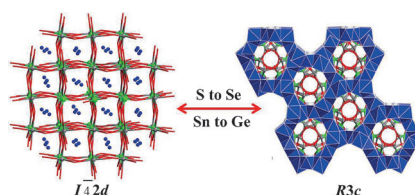
A Graphene Composite Material with Single Cobalt Active Sites: A Highly Efficient Counter Electrode for Dye-Sensitized Solar Cells



Inside Back Cover



Energy doubling: Four new nonlinear optical (NLO) materials were obtained and found to crystallize in two different space groups, namely $I4_2d$ (for compound Na_2BaSnS_4) and $R3c$ ($Na_2BaSnSe_4$, Na_2BaGeS_4 , and $Na_2BaGeSe_4$), constituting a novel tetragonal to trigonal structural transformation. The optical properties of Na_2BaSnS_4 and Na_2BaGeS_4 were found to meet the key requirements for IR NLO application.



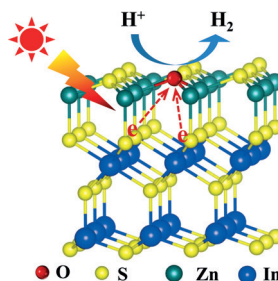
Nonlinear Optics

K. Wu, Z. Yang, S. Pan* — **6713–6715**

Na_2BaMQ_4 (M = Ge, Sn; Q = S, Se): Infrared Nonlinear Optical Materials with Excellent Performances and that Undergo Structural Transformations



Doping control: A model of ultrathin $ZnIn_2S_4$ nanosheets with oxygen doping offers insights into the influence of oxygen doping on the separation of photogenerated electron–hole pairs and the photocatalytic activity of catalysts at the atomic level. Experimental and theoretical studies reveal that the oxygen-doped $ZnIn_2S_4$ ultrathin nanosheets have enhanced photocatalytic activity.



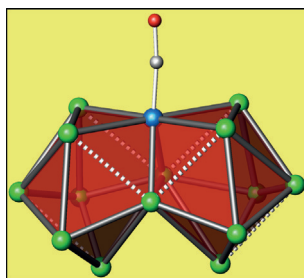
Hydrogen Evolution

W. L. Yang, L. Zhang, J. F. Xie, X. D. Zhang,* Q. H. Liu, T. Yao,* S. Q. Wei, Q. Zhang, Y. Xie* **6716–6720**

Enhanced Photoexcited Carrier Separation in Oxygen-Doped $ZnIn_2S_4$ Nanosheets for Hydrogen Evolution



Face to face: Two nine-atom clusters, each in the shape of a tricapped trigonal prism (the prismatic edges parallel to the three-fold axes are shown as broken lines), are “welded” at a triangular face made of two Sn and one Ni atoms to form $[Sn_{14}Ni(CO)]^{4-}$. The “welding” is achieved by heating of an ethylenediamine solution of the known clusters $[Ni@Sn_9Ni(CO)]^{3-}$.



Zintl Anions

L. G. Perla, S. C. Sevov* — **6721–6724**

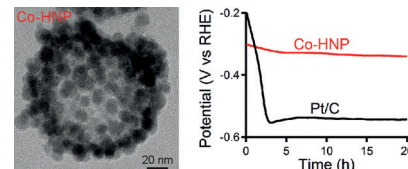
Cluster Fusion: Face-Fused Nine-Atom Deltahedral Clusters in $[Sn_{14}Ni(CO)]^{4-}$



Electrocatalysis

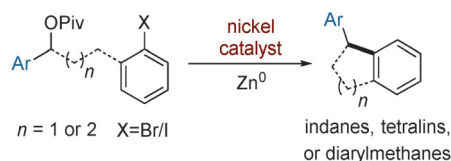
B. Liu, L. Zhang, W. Xiong,
M. Ma* 6725–6729Cobalt-Nanocrystal-Assembled Hollow
Nanoparticles for Electrocatalytic
Hydrogen Generation from Neutral-pH
Water

Our neutral friend: Fast electrochemical hydrogen generation from neutral-pH water is possible with an electrode composed of cobalt-nanocrystal-assembled hollow nanoparticles (Co-HNP) on a carbon cloth (CC). The Co-HNP/CC electrode retains its high activity after 20 h hydrogen generation at a high current density of 150 mAcm⁻².



Inside Cover

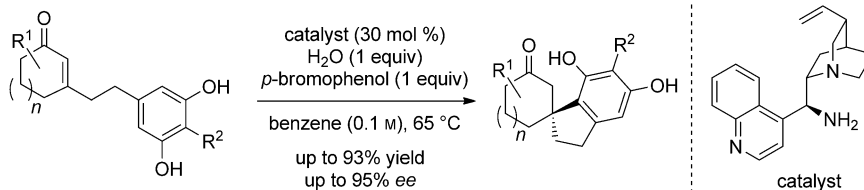
Cross-Coupling

M. O. Konev, L. E. Hanna,
E. R. Jarvo* 6730–6733Intra- and Intermolecular Nickel-
Catalyzed Reductive Cross-Electrophile
Coupling Reactions of Benzylic Esters with
Aryl Halides

Crossed off: Nickel-catalyzed cross-electrophile coupling reactions of benzylic esters and aryl halides have been developed. Both inter- and intramolecular variants proceed under mild reaction condi-

tions, and a range of heterocycles and functional groups are tolerated. Additionally, the first example of a stereospecific cross-electrophile coupling of a secondary benzylic ester is described.

Asymmetric Catalysis

K. Yoshida,* Y. Itatsu, Y. Fujino, H. Inoue,
K. Takao* 6734–6738Enantioselective Organocatalytic
Construction of Spiroindane Derivatives
by Intramolecular Friedel–Crafts-Type
1,4-Addition

Art and crafts: Intramolecular Friedel–Crafts-type 1,4-addition under organocatalytic conditions enabled the highly enantioselective construction of spiroindanes containing an all-carbon quater-

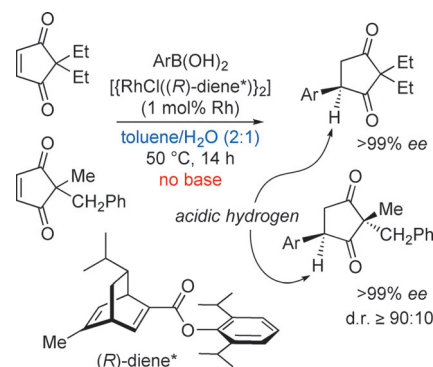
nary stereocenter. The reaction was applied to the asymmetric formal synthesis of the spirocyclic natural products (–)-cannabispirenone A and B (see scheme).

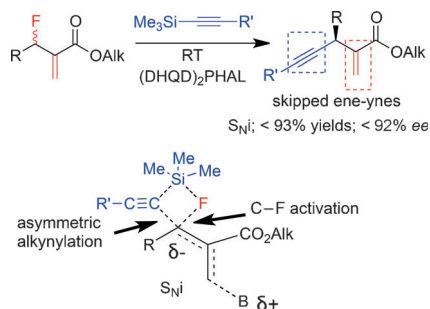
Asymmetric Catalysis

X. Dou, Y. Lu,* T. Hayashi* 6739–6743

Base-Free Conditions for Rhodium-
Catalyzed Asymmetric Arylation To
Produce Stereochemically Labile α -Aryl
Ketones**Forget about bases, score a home run:**

The asymmetric arylation of 2,2-dialkyl cyclopent-4-ene-1,3-diones with aryl boronic acids was efficiently catalyzed by a chiral diene–rhodium μ -chloro dimer without a base in toluene/H₂O (see scheme). The resulting α -aryl ketones can not be obtained with high ee values under the standard basic conditions for rhodium-catalyzed asymmetric arylation owing to their racemization in the presence of a base.



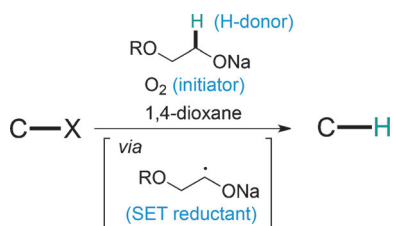


Chiral skipped ene-yne: An organocatalytic enantioselective alkynylation is reported based on Si/F activation of the allylic C–F bond. The reaction features a reasonably broad substrate scope, functional group tolerance, and neutral, mild, and operationally convenient reaction conditions.

Organocatalysis

S. Okusu, H. Okazaki, E. Tokunaga, V. A. Soloshonok, N. Shibata* ————— **6744–6748**

Organocatalytic Enantioselective Nucleophilic Alkynylation of Allyl Fluorides Affording Chiral Skipped Ene-yne

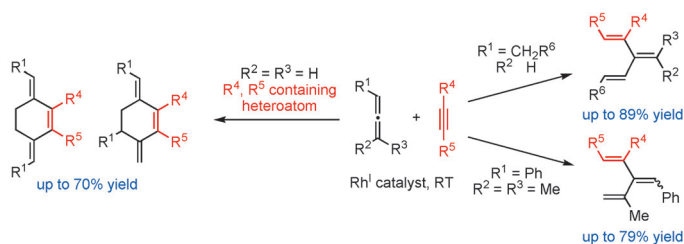


H-donor and e^- -donor: Alcoholates are used as cheap radical reducing reagents for the efficient reduction of various iodides. Chains are initiated by O_2 and alcoholates serve as efficient H-donors and one-electron reducing reagents in these electron-catalyzed chain reactions. Chemoselective hydrodeiodination over hydrodebromination is achieved.

Radical Reduction

A. Dewanji, C. Mück-Lichtenfeld, A. Studer* ————— **6749–6752**

Radical Hydrodeiodination of Aryl, Alkenyl, Alkynyl, and Alkyl Iodides with an Alcoholate as Organic Chain Reductant through Electron Catalysis



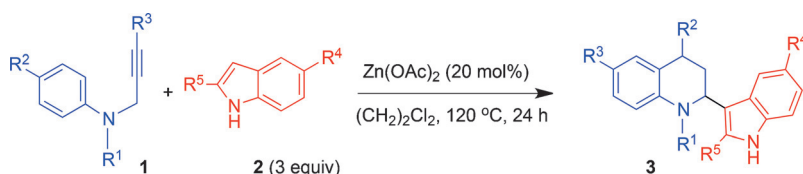
A triple cross: A cationic rhodium(I)/binap complex catalyzes the cross-cyclotrimerization of two molecules of a monosubstituted allene with one molecule of a functionalized alkyne to give 3,6-dialkylidenecyclohex-1-enes. In contrast,

the reactions involving di- or trisubstituted allenes and/or unfunctionalized alkynes afforded cross-dimerization products, substituted dendralenes. binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl.

Homogeneous Catalysis

K. Sakashita, Y. Shibata, K. Tanaka* ————— **6753–6757**

Rhodium-Catalyzed Cross-Cyclotrimerization and Dimerization of Allenes with Alkynes



Three C–H bonds (two sp^2 and one sp^3) are activated in one shot in the zinc(II)-catalyzed intramolecular hydroarylation-redox cross-dehydrogenative coupling

(CDC) of propargylic anilines with indoles to give 2-indolyltetrahydroquinolines in good to high yields.

C–H Activation

G. Li, H. Nakamura* ————— **6758–6761**

Synthesis of 2-Indolyltetrahydroquinolines by Zinc(II)-Catalyzed Intramolecular Hydroarylation-Redox Cross-Dehydrogenative Coupling of N-Propargylanilines with Indoles



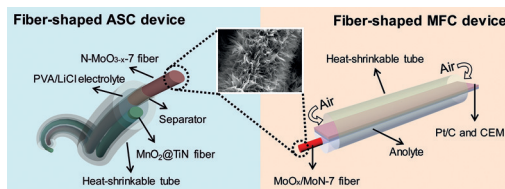


Energy Storage Materials

M. H. Yu, X. Y. Cheng, Y. X. Zeng,
Z. L. Wang, Y. X. Tong, X. H. Lu,*
S. H. Yang* — 6762–6766



Dual-Doped Molybdenum Trioxide
Nanowires: A Bifunctional Anode for
Fiber-Shaped Asymmetric
Supercapacitors and Microbial Fuel Cells



**High-performance fiber-shaped electro-
des:** A strategy for dual doping with
nitrogen and low-valent molybdenum
atoms was used to improve the electro-
chemical properties of MoO₃. The dual-

doped MoO₃ nanowires showed excep-
tional device performances as bifunc-
tional anode materials for both fiber-
shaped asymmetric supercapacitors
(ASCs) and microbial fuel cells (MFCs).

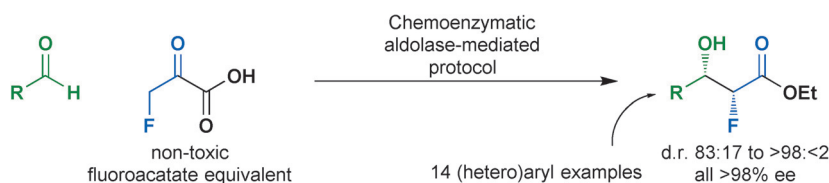
Chemoenzymatic Synthesis



J. K. Howard, M. Müller, A. Berry,*
A. Nelson* — 6767–6770



An Enantio- and Diastereoselective
Chemoenzymatic Synthesis of α -Fluoro
 β -Hydroxy Carboxylic Esters



Making high-quality building blocks: The
trans- α -hydroxybenzylidene pyruvate aldo-
lase-catalyzed reaction between fluoro-
pyruvate and many (hetero)aromatic
aldehydes yields aldol adducts without

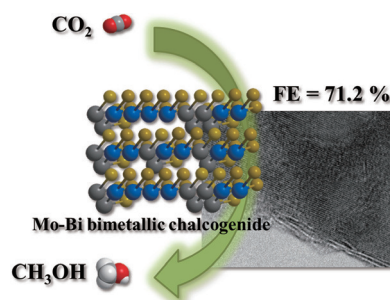
subsequent dehydration. Treatment of the
reaction products with hydrogen peroxide
gives the corresponding *syn*-configured α -
fluoro β -hydroxy carboxylic acids with
> 98% ee.

CO₂ Reduction

X. Sun, Q. Zhu, X. Kang, H. Liu, Q. Qian,
Z. Zhang, B. Han* — 6771–6775



Molybdenum–Bismuth Bimetallic
Chalcogenide Nanosheets for Highly
Efficient Electrocatalytic Reduction of
Carbon Dioxide to Methanol



MoBi thin: Mo-Bi bimetallic chalcogenide
nanosheets were utilized as an electro-
catalyst for CO₂ reduction to produce
methanol. The Faradaic efficiency (FE)
could reach 71.2% with a current density
of 12.1 mA cm⁻² in 0.5 M [Bmim]BF₄
MeCN solution, which are the highest
values to date.

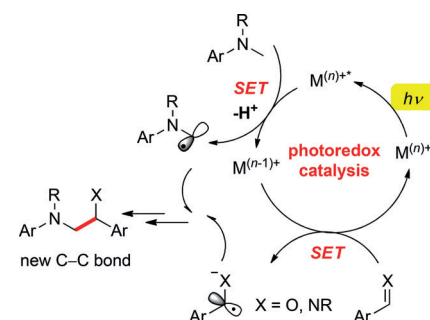
Photoredox Catalysis

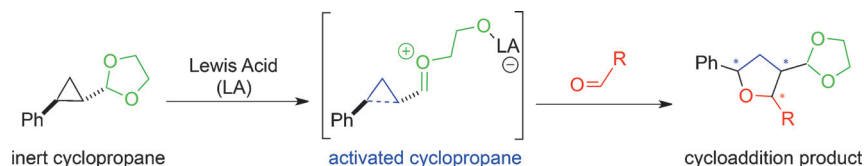
E. Fava, A. Millet, M. Nakajima,
S. Loescher, M. Rueping* — 6776–6779



Reductive Umpolung of Carbonyl
Derivatives with Visible-Light Photoredox
Catalysis: Direct Access to Vicinal
Diamines and Amino Alcohols via
 α -Amino Radicals and Ketyl Radicals

Anilines can be coupled with aldimines or
aldehydes in a visible-light-mediated
photoredox-catalyzed process. Reductive
single electron transfer (SET) umpolung
of the carbonyl derivatives leads to the
generation of intermediary ketyl and α -
amino radical anions, which were used for
the synthesis of unsymmetrically substi-
tuted 1,2-diamines and amino alcohols.





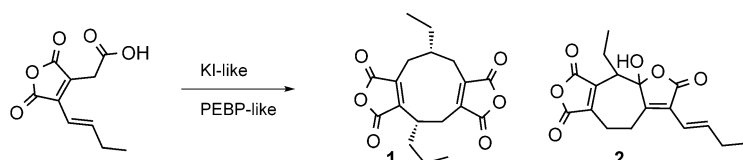
Hide-and-seek with a dipole: A novel formal [3+2] cycloaddition of cyclopropyl acetals and aldehydes was developed. This reaction affords trisubstituted tetrahydrofurans displaying three newly formed chiral centers with high diaste-

reoselectivity. The reaction relies on the transient generation of cyclopropyl oxocarbenium ions under mild conditions and is based on the concept of temporary activation of an otherwise inert protecting group.

Cycloaddition

J. Sabbatani, N. Maulide* — 6780–6783

Temporary Generation of a Cyclopropyl Oxocarbenium Ion Enables Highly Diastereoselective Donor–Acceptor Cyclopropane Cycloaddition



Ring cycle: The enzymes involved in the cyclization of the maleidride family of bioactive fungal natural products, including agnestadride A and byssochlamic acid, were identified. These previously

unknown proteins show homology to ketosteroid isomerases (KI-like) and phosphatidylethanolamine-binding proteins (PEBP-like).

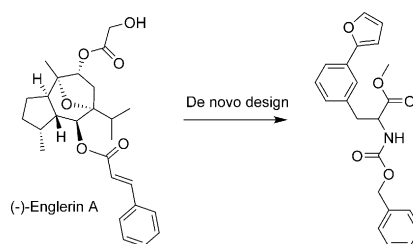
Biosynthesis

K. Williams,* A. J. Szwalbe, N. P. Mulholland, J. L. Vincent, A. M. Bailey, C. L. Willis, T. J. Simpson, R. J. Cox* — 6784–6788

Heterologous Production of Fungal Maleidrides Reveals the Cryptic Cyclization Involved in their Biosynthesis



Natural-product-inspired synthesis: Computer-based molecular design suggested synthetically accessible, low molecular weight compounds as mimetics of a complex natural product. The template Englerin A and the designed compounds potentially block TRPM8 channels, showing how computational design can be used to generate natural-product-inspired tool compounds for chemical biology and drug discovery.



Natural Product Mimetics

L. Friedrich, T. Rodrigues, C. S. Neuhaus, P. Schneider, G. Schneider* — 6789–6792

From Complex Natural Products to Simple Synthetic Mimetics by Computational De Novo Design



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

^2H and ^{139}La NMR Spectroscopy in Aqueous Solutions at Geochemical Pressures

G. Ochoa, C. D. Pilgrim, M. N. Martin, C. A. Colla, P. Klavins, M. P. Augustine, W. H. Casey* **15444–15447**

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

DOI: 10.1002/anie.201507773

In Figure 1 of this Communication, the units on the vertical axes were incorrectly given as milliseconds instead of seconds. The corrected Figure 1 is shown below. The authors apologize for this oversight.

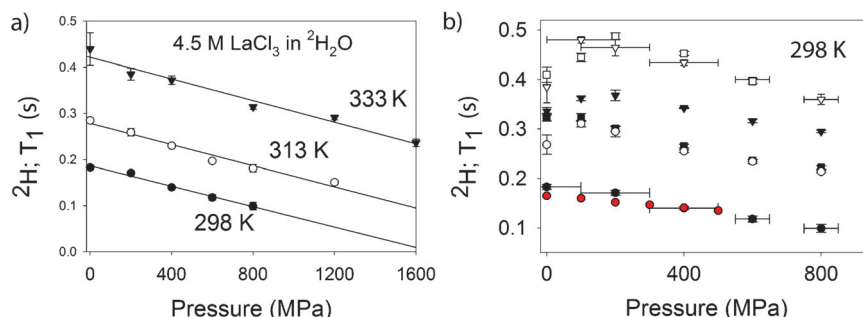
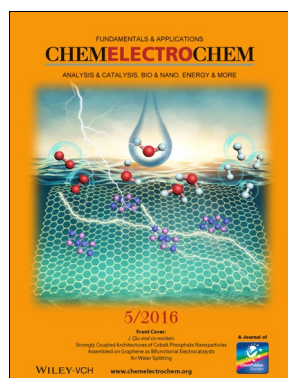
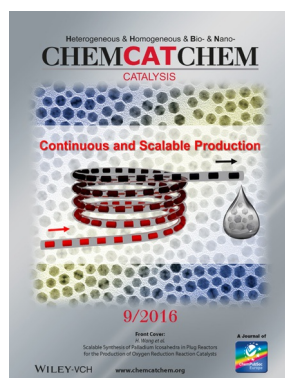


Figure 1. a) T_1 values from ^2H NMR spectra as a function of pressure of 4.5 M $\text{LaCl}_3 + ^2\text{H}_2\text{O}$ solutions. The lines are linear regressions. The T_1 values as a function of solution composition at 298 K are shown in (b). The solid circles (●) are 4.5 M LaCl_3 and the red symbols (●) identify data of Lee et al. (1974).^[5] The $\text{LaCl}_3 + ^2\text{H}_2\text{O}$ solutions are: ○ = 1.0 M, ▼ = 0.5 M, ▽ = 0.1 M, and the $\text{La}(\text{ClO}_4)_3 + ^2\text{H}_2\text{O}$ solutions are: ■ = 1.0 M and □ = 0.1 M. Uncertainties in pressure are ± 100 MPa at 400 MPa or less and 50 MPa at pressures higher than 400 MPa. They are shown only for the 0.1 M and 4.5 M LaCl_3 data to avoid clutter and are assigned as the 95 % prediction interval from repeated external calibrations (see the Supporting Information).

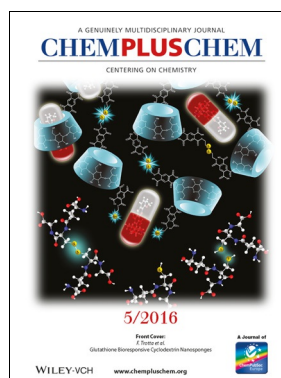
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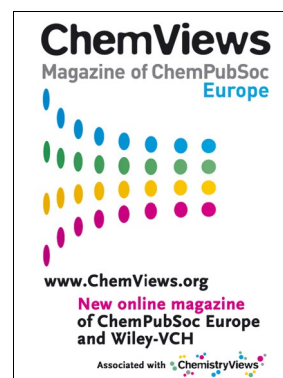
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