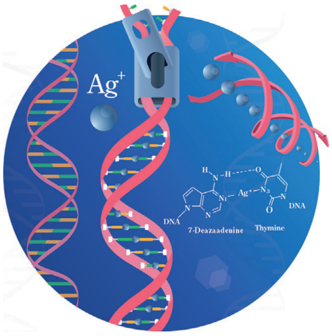
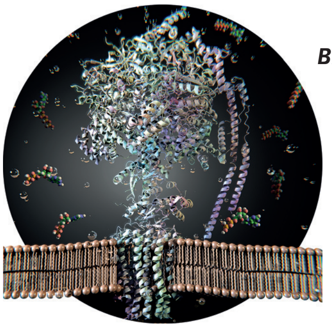
It takes two to tango

The production of the energy carrier and platform chemical methanol by CO_2 hydrogenation is expected to become a key step in a sustainable economy but the realization of this process requires high-performance catalysts. In their Communication on page 6261 ff., J. Pérez-Ramírez and co-workers demonstrate that the synergistic interaction of In_2O_3 and a ZrO_2 carrier leads to a highly stable material that provides methanol in high space time yields and with almost 100 % selectivity.

DNA Structures

In their Communication on page 6170 ff., M. A. Galindo et al. substitute hydrogen bonds in a double-stranded oligonucleotide comprising Watson–Crick-paired 7-deazaadenine and thymine with silver(I) coordination bonds.



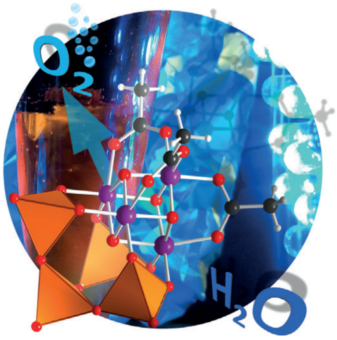


Biomimetic Systems

A. L. De Lacey, M. Vélez, and co-workers show in their Communication on page 6216 ff. that ATP synthesis is achieved by the F_1F_0-ATP synthase immobilized within a lipid bilayer covering a gold electrode.

Water Oxidation

A molecular manganese vanadium oxide that resembles the oxygen-evolving complex in photosystem II was used for visible-light-driven water oxidation catalysis by C. Streb and co-workers in their Communication on page 6329 ff.



How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

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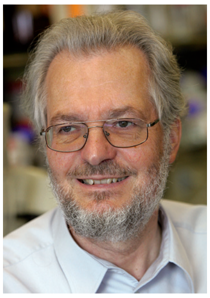
Editorial

“... Despite the introduction of high-throughput and combinatorial methods that certainly can be useful in the process of catalysts optimization, it is recognized that the generation of fundamental knowledge at the molecular level is key for the development of new concepts and for reaching the final objective of solid catalysts by design ...”
Read more in the Editorial by Avelino Corma.

Service

Author Profile



“My favorite author (fiction) is Philip Roth.
My favorite place on earth is a Japanese garden in Kyoto such as Ginkaku-ji ...”
This and more about Horst Kessler can be found on page 6132.

News

P. Strasser

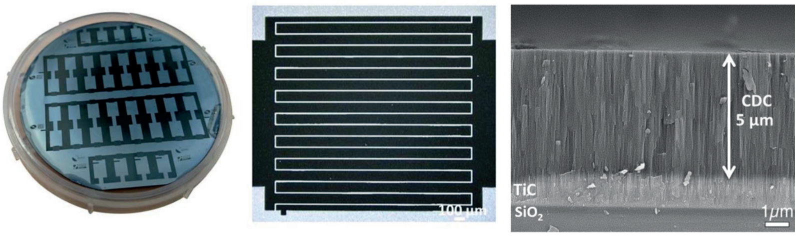
H. Tüysüz

S. E. Skrabalak

T. M. Swager

Highlights

Carbon Materials

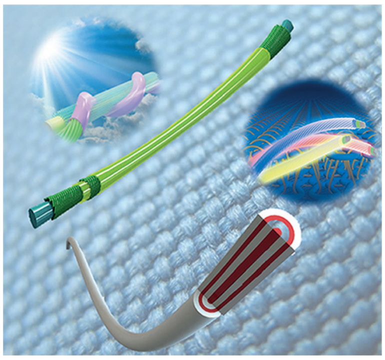


CSi electronics: Recently, Simon and co-workers demonstrated silicon-wafer-supported elastic carbide-derived carbons (CDCs) films without any delamination or cracks for micro-supercapacitor application. The fabrication of these CDC films is particularly important for the practical application of micro-supercapacitors in silicon-based electronics and flexible electronics.

Reviews

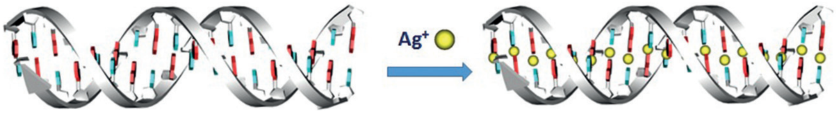
Electronic Textiles

Working clothes: Electronic textiles are a promising technology that could soon become part of our everyday lives. The three typical functions of wearable electronics—generation, storage, and utilization of electricity—are discussed with a main focus on functional materials.



Communications

DNA Structures

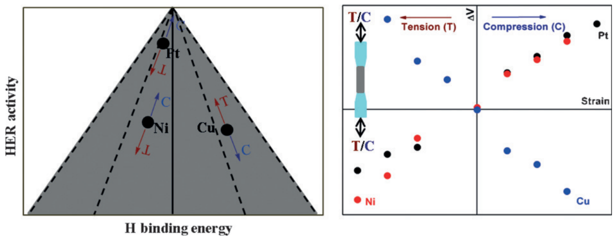


Substitution of the original hydrogen bonds by silver(I) coordination bonds in a double-stranded oligonucleotide comprising Watson–Crick-paired 7-deazaadenine and thymine nucleobases leads to a sequential array of metal-mediated base pairs. The stability of the silver-containing structure was significantly higher than that of the parent compound while the double-helix structure was retained.

Frontispiece

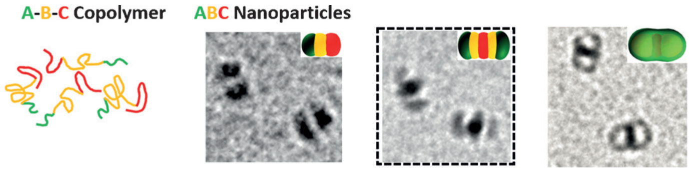
For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 101161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 16.862/14.051 (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.

Catalyst Design



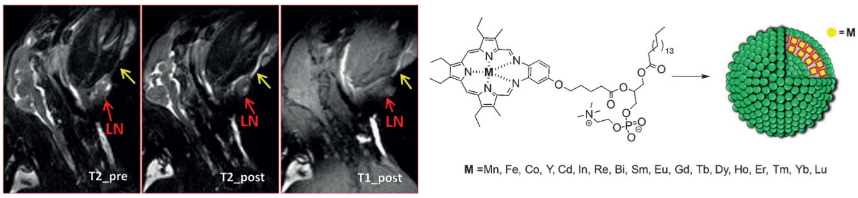
Strain-tuned catalysis: Elastic strain affects catalytic reaction rates, but is often coupled with a ligand effect. To isolate the strain effect, three thin metal films on elastic substrates were subjected to uniaxial loading and unloading, and investigated for their activity in the hydrogen evolution reaction.

Hierarchical Nanoparticles



As easy as ABC: Narrow-disperse ABC three-segment hierarchical nanostructured polymeric nanoparticles (HNPs) with a size of tens of nm were prepared through solution-based hierarchical self-assembly of an A-*b*-B-*b*-C triblock copolymer. Further self-assembly of the ABC HNPs resulted in narrow-disperse NPs with a Θ-like morphology.

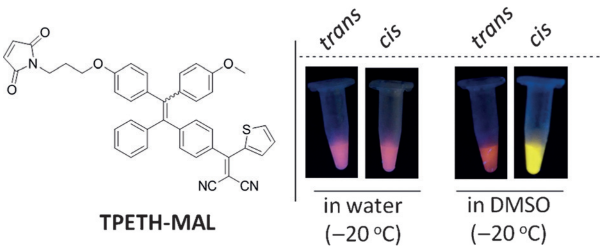
Imaging Agents



Contrast and compare: A one-pot synthesis and self-assembly method is described for preparation of Mn-texaphyrin-phospholipids, allowing facile self-assembly of Mn-nanotexaphyrins. Each Mn-nanotexaphyrin constitutes a stable 1:1 porphyrin:metal chelation, equating to 8×10^4 Mn^{II} ions. The newly prepared contrast agent was applied to magnetic resonance imaging (MRI) of lymphatic metastasis drainage, revealing drainage from the tumor site to the adjacent metastatic lymph node.

Aggregation-Induced Emission

VIP

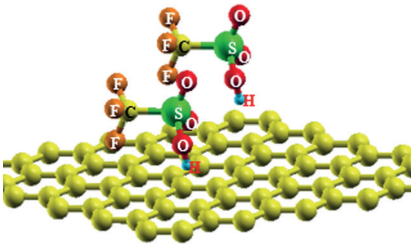


The *cis* and *trans* isomers of a tetraphenylethene derivative with aggregation-induced emission, TPETH-MAL, were characterized by HPLC analysis and NMR spectroscopy. *cis*-TPETH-MAL emits yellow fluorescence in DMSO at −20 °C whereas *trans*-TPETH-MAL shows red fluorescence under the same conditions.

Flexible OLED

T.-H. Han, S.-J. Kwon, N. Li, H.-K. Seo, W. Xu, K. S. Kim, T.-W. Lee* **6197 – 6201**

Versatile p-Type Chemical Doping to Achieve Ideal Flexible Graphene Electrodes

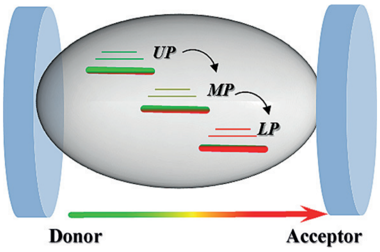


Anodic optimization: p-Type chemical doping of graphene with trifluoromethanesulfonic acid (TFMS) leads to a flexible graphene anode with 70% reduced sheet resistance and 0.83 eV increased surface work function with excellent air-stability. An OLED with TFMS-doped graphene anode exhibited lower operating voltage and higher efficiency than those with conventional ITO anode.

Energy Transfer

X. Zhong, T. Chervy, S. Wang, J. George, A. Thomas, J. A. Hutchison, E. Devaux, C. Genet, T. W. Ebbesen* **6202 – 6206**

Non-Radiative Energy Transfer Mediated by Hybrid Light-Matter States

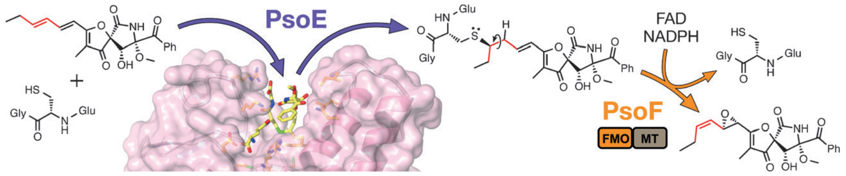


When the donor and acceptor are hybridized with the vacuum field of an optical cavity non-radiative energy transfer is enhanced. Strong coupling of the donor resonant with a cavity mode, and then with the acceptor, leads to the formation of three new eigen hybrid light-matter states: the upper (UP), middle (MP), and lower (LP), polaritonic states.

Polyketides

T. Yamamoto, Y. Tsunematsu, K. Hara, T. Suzuki, S. Kishimoto, H. Kawagishi, H. Noguchi, H. Hashimoto, Y. Tang, K. Hotta, K. Watanabe* **6207 – 6210**

Oxidative *trans* to *cis* Isomerization of Olefins in Polyketide Biosynthesis

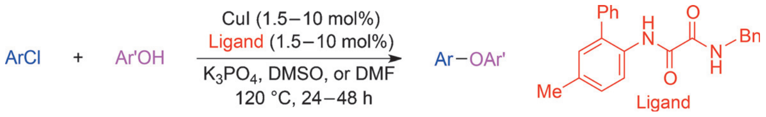


Strike a 'PsoE': An in vitro study revealed that the glutathione S-transferase PsoE required the bifunctional PsoF to complete the isomerization of a pseurotin biosynthetic pathway intermediate. The PsoE crystal structure indicated that the intermediate–glutathione conjugation to be the sole function of PsoE. PsoF was identified to have an additional oxidative isomerase activity, thus making it a trifunctional enzyme which is key to generating complexity in pseurotin biosynthesis.

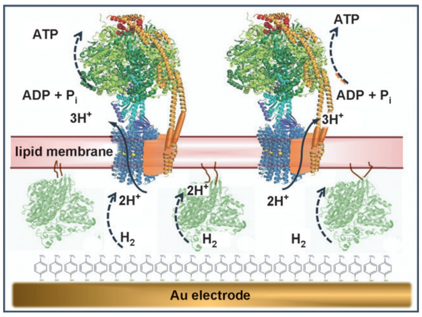
Cross-Coupling

M. Fan, W. Zhou, Y. Jiang, D. Ma* **6211 – 6215**

CuI/Oxalamide Catalyzed Couplings of (Hetero)aryl Chlorides and Phenols for Diaryl Ether Formation



Aryl and alkyl: N-Aryl-N′-alkyl-substituted oxalamide ligands promote the CuI catalyzed coupling of (hetero)aryl chlorides and phenols at 120 °C more effectively than bis(N-aryl)-substituted oxalamides. A wide range of electron-rich and electron-poor aryl and heteroaryl chlorides were converted into the corresponding coupling products in good yields.



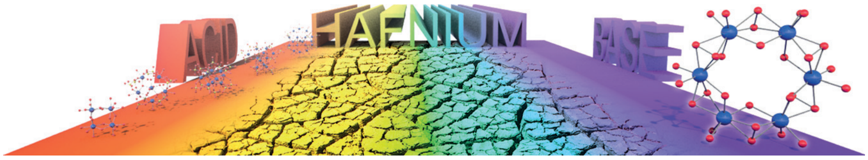
ATP synthesis fueled by H_2: A gold electrode modified with an oriented membrane-bound NiFeSe hydrogenase, a lipid membrane, and an integrated F_1F_0-ATPase generates a local proton gradient by electroenzymatic H_2 oxidation, which is then used to synthesize ATP. This electrode-assisted conversion of H_2 into ATP could locally generate biochemical fuel in medical devices or enzymatic synthesis.

Biomimetic Systems

Ó. Gutiérrez-Sanz, P. Natale, I. Márquez, M. C. Marques, S. Zacarias, M. Pita, I. A. C. Pereira, I. López-Montero,* A. L. De Lacey,* M. Vélez* **6216 – 6220**

H_2-Fueled ATP Synthesis on an Electrode: Mimicking Cellular Respiration

Inside Back Cover



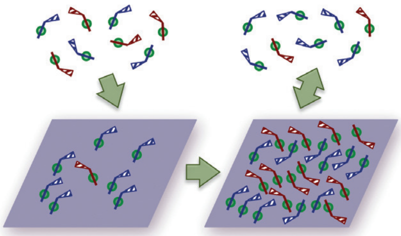
Crossing the amphoteric desert: Beyond the acidic region, the chemistry of hafnium oxo-hydroxo clusters has been a barren landscape. The first hafnium polynuclear hydroxo cluster was now isolated from basic solution, and it has surprising similarities to clusters isolated on the opposite end of the pH scale.

Cluster Compounds

S. Goberna-Ferrón, D.-H. Park, J. M. Amador, D. A. Keszler, M. Nyman* **6221 – 6224**

Amphoteric Aqueous Hafnium Cluster Chemistry

To enantioenrich or not to enantioenrich? The adsorption of propylene oxide on Pt(111) surfaces shows an initial kinetic preference for the formation of enantiopure layers, but that trend reverses at saturation, at which point an enhanced racemization is observed.

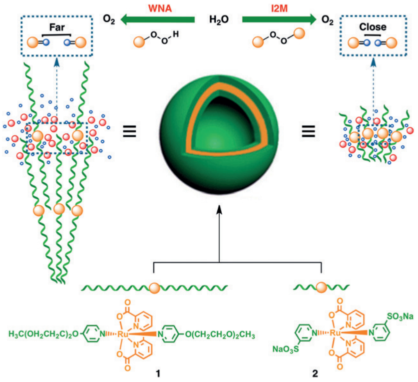


Chiral Amplification

S. Karakalos, J. Hong, F. Zaera* **6225 – 6228**

Changes in the Enantiomeric Composition of Chiral Mixtures Upon Adsorption on a Non-Chiral Surface

Making contacts: Amphiphilic complexes **1** and **2** self-assemble into vesicle-like particles in water. The different hydrophilic axial ligands lead to different valence states and aggregation patterns of the Ru species for water oxidation. This is the first example for the regulation of O—O bond formation through supramolecular interaction of ancillary ligands.



Water Oxidation

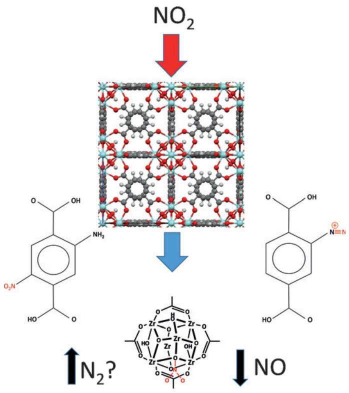
B. Yang, X. Jiang, Q. Guo, T. Lei, L.-P. Zhang, B. Chen, C.-H. Tung, L.-Z. Wu* **6229 – 6234**

Self-Assembled Amphiphilic Water Oxidation Catalysts: Control of O—O Bond Formation Pathways by Different Aggregation Patterns

Air Filtration

G. W. Peterson,* J. J. Mahle, J. B. DeCoste, W. O. Gordon, J. A. Rossin **6235 – 6238**

Extraordinary NO_2 Removal by the Metal–Organic Framework UiO-66-NH_2

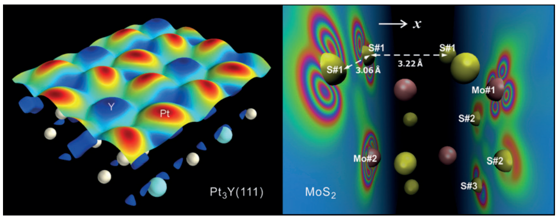


Clean air with MOF: The metal–organic framework UiO-66-NH_2 was used to remove toxic nitrogen dioxide from streams of air with only small amounts of nitric oxide formed. The highly efficient reaction was due to formation of several nitrate species, as well as a diazonium ion on the MOF secondary building unit. It is also possible that molecular nitrogen was formed during the reaction.

Electronic Surface Properties

B. Huang, L. Xiao, J. Lu, L. Zhuang* **6239 – 6243**

Spatially Resolved Quantification of the Surface Reactivity of Solid Catalysts

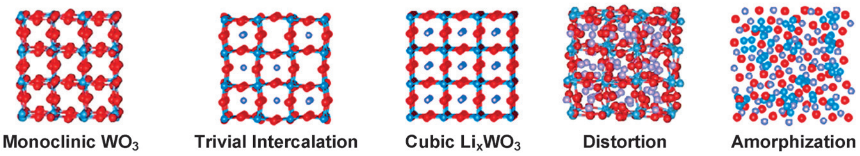


Just a big softy: Fermi softness is proposed as a new electronic property of the solid surface, which is quantitatively related to the surface reactivity and also allows reactivity imaging with atomistic resolution. The core idea is to use a reactivity weight function peaking at the Fermi level for weighted summation of the density of states of a solid surface.

Ion Batteries

Y. He, M. Gu, H. Xiao, L. Luo, Y. Shao, F. Gao,* Y. Du,* S. X. Mao,* C. Wang* **6244 – 6247**

Atomistic Conversion Reaction Mechanism of WO_3 in Secondary Ion Batteries of Li, Na, and Ca

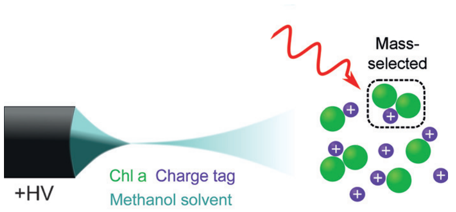


The interplay between ion intercalation and WO_3 battery electrode conversion was investigated at atomic scale by using in situ HRTEM. The ion–oxygen bond formation destabilizes the WO_3 framework which gradually shrinks, distorts and finally collapses to an amorphous W and M_xO (M = Li, Na, Ca) composite structure.

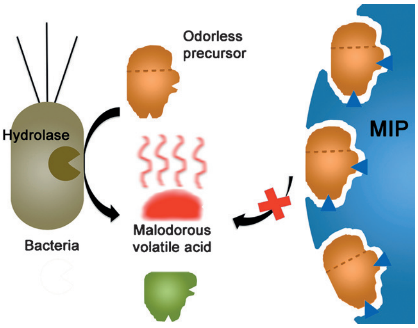
Chlorophyll

B. F. Milne,* C. Kjær, J. Houmøller, M. H. Stockett, Y. Toker, A. Rubio, S. B. Nielsen* **6248 – 6251**

On the Exciton Coupling between Two Chlorophyll Pigments in the Absence of a Protein Environment: Intrinsic Effects Revealed by Theory and Experiment



How strong is the coupling between two adjacent chlorophyll molecules in the absence of a protein environment? Mass spectrometry experiments now provide an answer to this question as chlorophyll a dimers tagged by quaternary ammonium ions could be produced in the gas phase by electrospray ionization.



A new deodorant principle: Molecularly imprinted polymers (MIPs) are used for the first time as active ingredients in a cosmetic product, for suppressing body odors. In a dermo-cosmetic formulation, the MIP captures the precursors of malodorous compounds in human sweat, thus preventing them from being transformed into odorous molecules.

Fighting Body Odor

S. Nestora, F. Merlier, S. Beyazit, E. Prost, L. Duma, B. Baril, A. Greaves, K. Haupt,* B. Tse Sum Bui* ____ **6252 – 6256**

Plastic Antibodies for Cosmetics: Molecularly Imprinted Polymers Scavenge Precursors of Malodors

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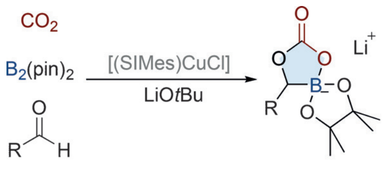

- > 18 examples, up to 91% yields
- > highly selective four-component coupling
- > novel catalytic process for CO_2 fixation
- > new lithium cyclic boracarbonates

A novel family of well-defined molecular lithium boracarbonate ion pairs containing a unique boron-implanted cyclic carbonate framework are efficiently synthesized by the highly selective coupling reaction of CO_2, bis(pinacolato)diboron, LiO*t*Bu, and a wide range of aldehydes in the presence of an N-heterocyclic carbene copper catalyst.

Cyclic Boracarbonates

B. Carry, L. Zhang,* M. Nishiura, Z. Hou* ____ **6257 – 6260**

Synthesis of Lithium Boracarbonate Ion Pairs by Copper-Catalyzed Multi-Component Coupling of Carbon Dioxide, Diboron, and Aldehydes

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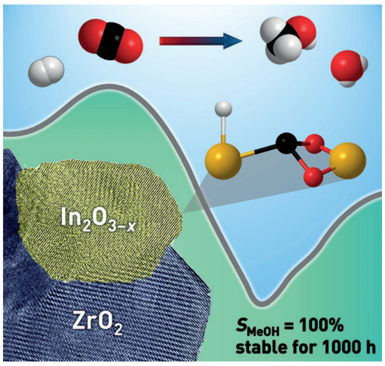
Surface oxygen vacancies in indium oxide drive the selective hydrogenation of CO_2 to methanol. Strong electronic interactions between this active phase and the ZrO_2 carrier and further vacancy formation by CO co-feeding lead to excellent catalytic activity.

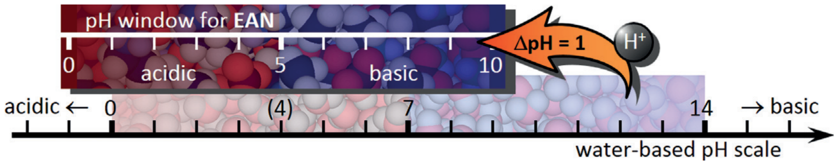


Methanol Synthesis

O. Martin, A. J. Martín, C. Mondelli, S. Mitchell, T. F. Segawa, R. Hauert, C. Drouilly, D. Curulla-Ferré, J. Pérez-Ramírez* ____ **6261 – 6265**

Indium Oxide as a Superior Catalyst for Methanol Synthesis by CO_2 Hydrogenation

Front Cover



Tipping the pH scale: By using potentiometric acid–base titrations, a pH scale applicable to the protic ionic liquid ethylammonium nitrate (EAN) was determined. This water-based pH scale can be employed to directly compare the differences in H^+ activity between EAN and water. For example, the H^+ activity in the neutral EAN corresponds to the aqueous solution with pH = 4.

Protic Ionic Liquids

R. Kanzaki,* H. Kodamatani, T. Tomiyasu, H. Watanabe, Y. Umebayashi* ____ **6266 – 6269**

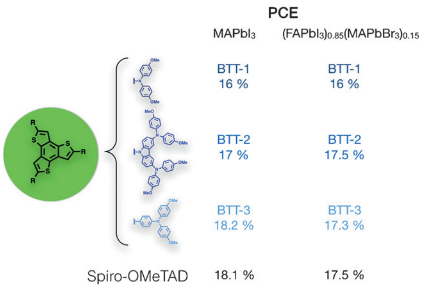
A pH Scale for the Protic Ionic Liquid Ethylammonium Nitrate

Solar Cells

A. Molina-Ontoria, I. Zimmermann,
I. Garcia-Benito, P. Gratia,
C. Roldán-Carmona, S. Aghazada,
M. Graetzel, M. K. Nazeeruddin,*
N. Martín* ———— **6270 – 6274**

Benzotrithiophene-Based Hole-Transporting Materials for 18.2% Perovskite Solar Cells

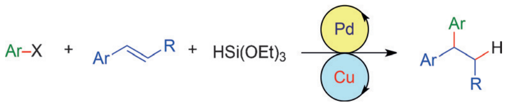
Promising new candidates: Benzotrithiophenes (BTT) with different donor moieties are introduced as hole-transporting materials for perovskite solar cells. The incorporation of these new derivatives in photovoltaic devices leads to power conversion efficiencies (PCE) up to 18.2%, thus paving the way to very efficient and highly versatile materials for light-energy conversion.



Alkenes

K. Semba,* K. Ariyama, H. Zheng,
R. Kameyama, S. Sakaki,*
Y. Nakao* ———— **6275 – 6279**

Reductive Cross-Coupling of Conjugated Arylalkenes and Aryl Bromides with Hydrosilanes by Cooperative Palladium/Copper Catalysis

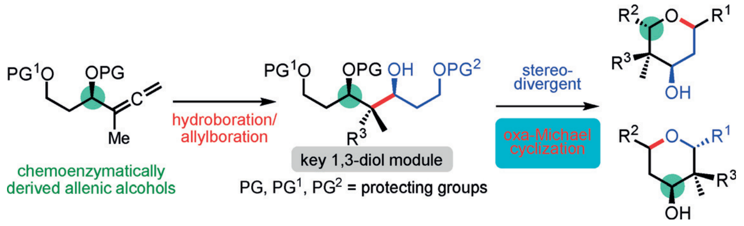


Forming a Co-op: A method for the reductive cross-coupling of conjugated arylalkenes or internal alkynes and aryl bromides with hydrosilanes using cooperative palladium/copper catalysis was developed. The resulting 1,1-diarylalkanes and trisubstituted alkenes were isolated with high regio- and stereoselectivity. Under the applied reaction conditions, high levels of functional-group tolerance were observed.

Tetrahydropyranes

L. Yang, Z. Lin, S.-H. Huang,*
R. Hong* ———— **6280 – 6284**

Stereodivergent Synthesis of Functionalized Tetrahydropyrans Accelerated by Mechanism-Based Allylboration and Bioinspired Oxa-Michael Cyclization

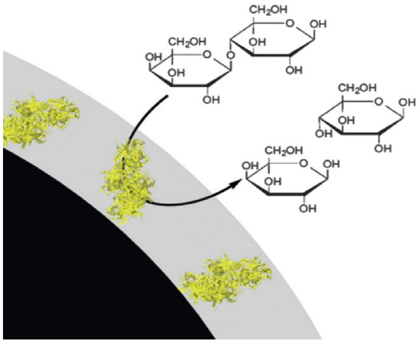


Symmetry breakdown: The thermodynamic and kinetic hydroboration of allenes and subsequent allylboration provide a key stereodefinable module with a latent symmetry. Following a deprotection/chain elongation/oxa-Michael cyclization sequence, the stereocogeners of highly functionalized tetrahydropyrans were synthesized for rapid access to structural motifs found in bioactive polyketides.

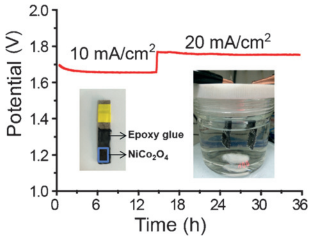
Nanobiocatalysts

M. R. Correro, N. Moridi, H. Schützinger,
S. Sykora, E. M. Ammann, E. H. Peters,
Y. Dudal, P. F. X. Corvini,
P. Shahgaldian* ———— **6285 – 6289**

Enzyme Shielding in an Enzyme-thin and Soft Organosilica Layer



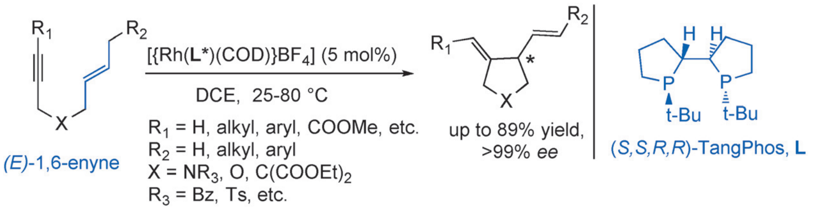
Important soft skills: Hybrid organic/inorganic nanobiocatalysts were created by the immobilization of enzymes on amino-modified silica nanoparticles and subsequent self-assembly and polycondensation of silane building blocks at the surface of the enzymes. The soft environment of the organosilica layer shielded the enzymes from denaturing stresses; however, the enzymes retained their conformational freedom and thus their catalytic activity (see picture).



Form an orderly cuboid: Prepared in a simple hydrothermal reaction, hollow $NiCo_2O_4$ microcuboids constructed from 1D porous nanowire subunits, function as highly active and stable electrode materials for high-performance overall water-splitting. 10 $mA\,cm^{-2}$ water-splitting current is reached by applying just 1.65 V and 20 $mA\,cm^{-2}$ by just 1.74 V across the two electrodes.

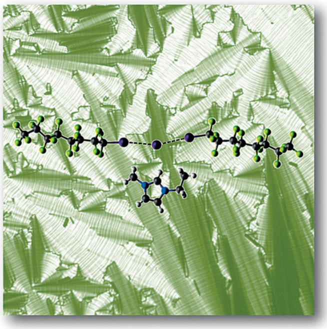
Water Splitting

Inside Cover



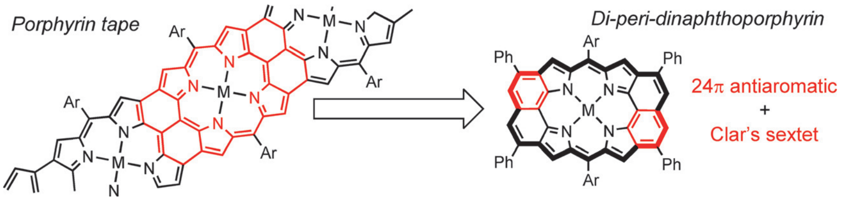
A solution after 15 years: The first rhodium(I)-catalyzed asymmetric cycloisomerization reaction of challenging (*E*)-configured 1,6-enyes is reported. The reaction provides access to five-membered carbo- and heterocycles with excellent enantioselectivity. DFT studies provide a rationale for the striking reactivity difference between (*E*)- and (*Z*)-1,6-enynes using Rh^I-BINAP and Rh^I-TangPhos.

Asymmetric Synthesis



Out of the ordinary: The high directionality of halogen bonds and the fluorophobic effect were exploited in the design and synthesis of a new family of unconventional superfluorinated ionic liquid crystals. The liquid crystallinity of the system is driven by halogen-bonded supramolecular anions $[C_nF_{2n+1}\text{-I}\cdots\text{I}\cdots\text{I-}C_nF_{2n+1}]^-$ which act as rigid rod-like calamitic units.

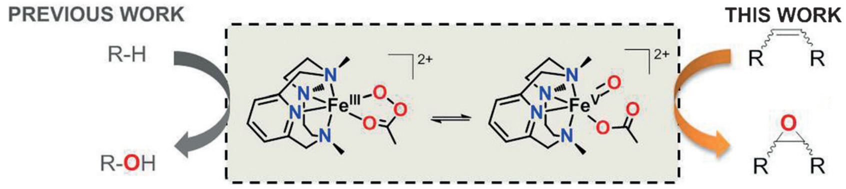
Ionic Liquid Crystals



The core of the matter: Di-*peri*-dinaphthoporphyrins have been synthesized by $PtCl_2$-mediated cycloisomerization reaction of quinodimethane-type porphyrins. These porphyrins can be regarded as a key substructure of fused porphyrinoids, for which a 24π antiaromatic circuit was proven to be a dominant resonance contributor by ^1H NMR, UV/Vis absorption, cyclic voltammetry, NICS calculations, and AICD plot.

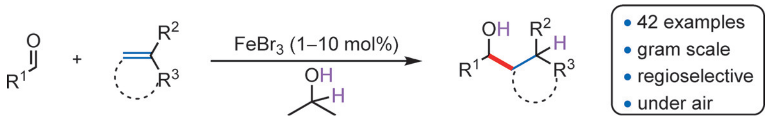
Porphyrins

Iron–Oxygen Species



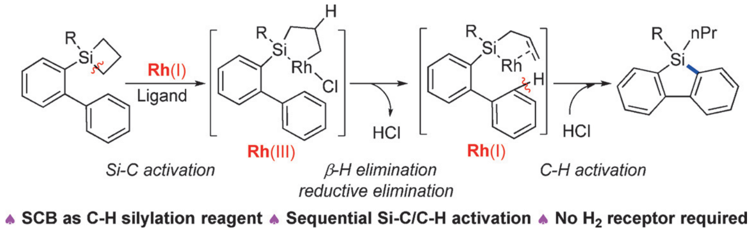
A metastable nonheme iron–oxygen species undergoes exceedingly fast oxygen atom transfer (OAT) to olefins, providing epoxides with stereoretention. The reaction rates determined by stopped-flow UV/Vis analysis are in good agreement with the relative reactivities of different olefins, confirming that this compound is a competent OAT intermediate of relevance to nonheme iron catalyzed epoxidations.

Transfer Hydrogenative Couplings



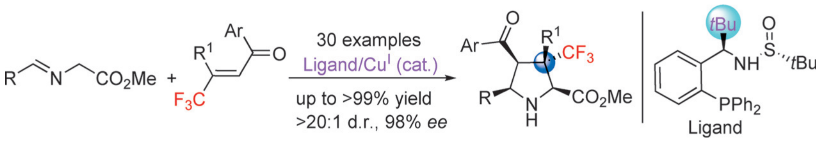
The reductive coupling of various aldehydes and alkenes through a direct hydride transfer pathway can be catalyzed by $FeBr_3$. With isopropanol as the hydrogen donor, previously challenging coupling reactions of unactivated alkyl and aryl aldehydes with simple alkenes, such as styrene derivatives and α-olefins, proceeded smoothly to furnish a diverse range of functionalized alcohols with complete linear regioselectivity.

C—H Activation



Old reagent, new reactivity: Silacyclobutane was discovered to be an efficient C—H bond silylation reagent under the catalysis of Rh/TMS-segophos. This new reactivity was attributed to a key Si—Rh^I intermediate formed through a Si—C activation, endocyclic β-H elimination and reductive elimination cascade. A wide array of siloles was obtained in high yields and excellent regioselectivities.

Cycloadditions



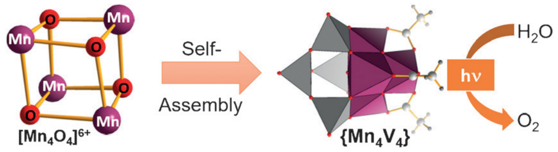
Out on pyrrol(idine): An asymmetric [3+2] cycloaddition reaction of azomethine ylides with β-trifluoromethyl β,β-disubstituted enones is enabled by the copper(I) catalyst with Ming-Phos ligand. The highly substituted product pyrrolidines, having a trifluoromethylated, all-carbon quaternary stereocenter, are isolated in good yields with up to greater than 20:1 d.r. and 98% *ee*.

Water Oxidation

B. Schwarz, J. Forster, M. K. Goetz, D. Yücel, C. Berger, T. Jacob, C. Streb* ______ **6329 – 6333**

Visible-Light-Driven Water Oxidation by a Molecular Manganese Vanadium Oxide Cluster

Back Cover

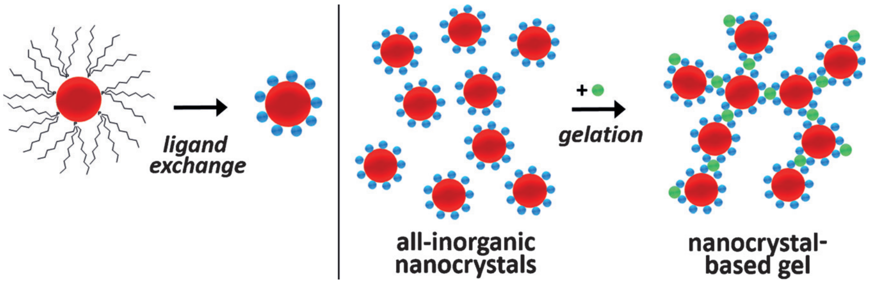


A molecular manganese vanadium oxide cluster was synthesized, characterized, and employed as a catalyst for visible-light-driven water oxidation. The compound is a molecular model for the oxygen evolving complex (OEC) in photosystem II and provides access to the S_1, S_2, and S_3 redox states of the water oxidation ("Kok") cycle.

Nanocrystal Assemblies

V. Sayevich, B. Cai, A. Benad, D. Haubold, L. Sonntag, N. Gaponik, V. Lesnyak,* A. Eychmüller ______ **6334 – 6338**

3D Assembly of All-Inorganic Colloidal Nanocrystals into Gels and Aerogels

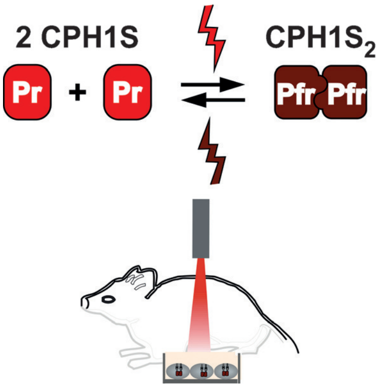


An assembly approach for a variety of electrostatically stabilized all-inorganic semiconductor nanocrystals is based on their linking with appropriate ions into multibranched gel networks. The resulting aerogels are highly porous monolithic structures, which preserve the quantum confinement of their building blocks.

Optogenetics

E. Reichhart, A. Ingles-Prieto, A.-M. Tichy, C. McKenzie, H. Janovjak* _ **6339 – 6342**

A Phytochrome Sensory Domain Permits Receptor Activation by Red Light



Go deep with red: The sensory domain (S) of the cyanobacterial phytochrome 1 (CPH1) was repurposed to induce the homodimerization of proteins in living cells by red light. By using this domain, light-activated protein kinases were engineered that can be activated orthogonally from many fluorescent proteins and through mammalian tissue. Pr/Pfr = red-/far-red-absorbing state of CPH1.

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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