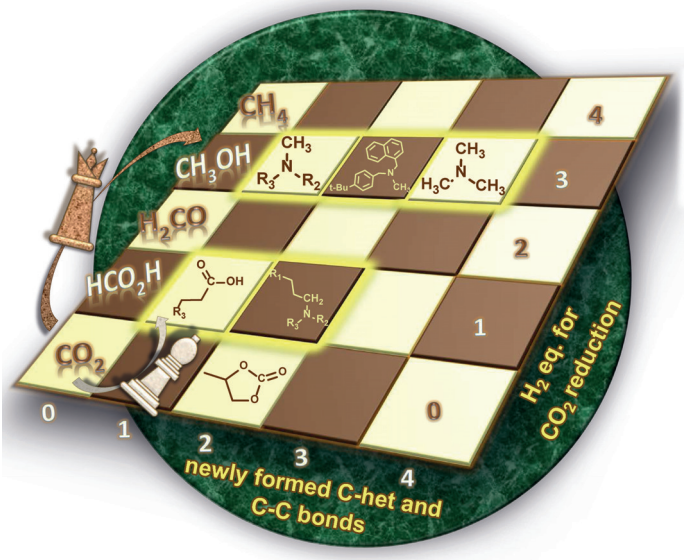
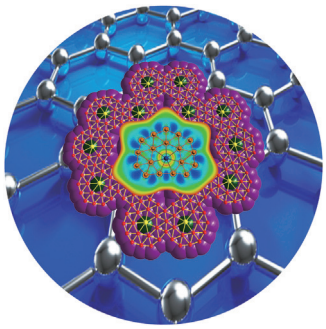
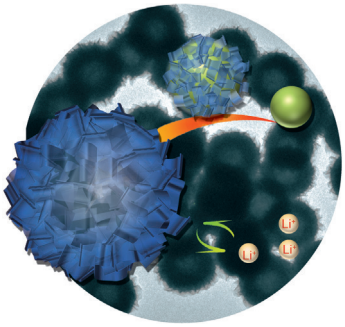


… as building blocks offers attractive synthetic pathways ranging from large-volume base chemicals to highly functionalized complex molecules. J. Klankermayer, W. Leitner et al. describe in their Review on page 7296 ff. how efficient catalysts are becoming available to master the bond breaking and bond formation events required for these processes like strategic moves on a molecular chess board.



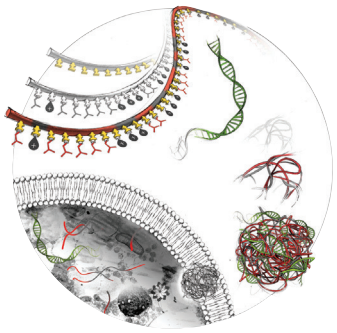
Metalloborophenes

The CoB_{18}^- cluster is investigated by J. Li, L.-S. Wang et al. in their Communication on page 7358 ff. It is a highly stable and perfectly planar structure with the Co atom centered in a seven-membered ring.



Hierarchical Nanomaterials

In their Communication on page 7423 ff. X. W. Lou et al. prepare hierarchical spherical MoS_2 structures that are formed from ultrathin subunits and have a hollow interior. They are promising anode materials for lithium-ion batteries.



siRNA Delivery

The post-polymerization functionalization of a polyhydrazide scaffold to produce amphiphilic vectors for polynucleotide delivery is reported by J. Montenegro, F. Fernandez-Trillo et al. in their Communication on page 7492 ff.

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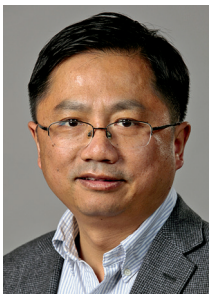
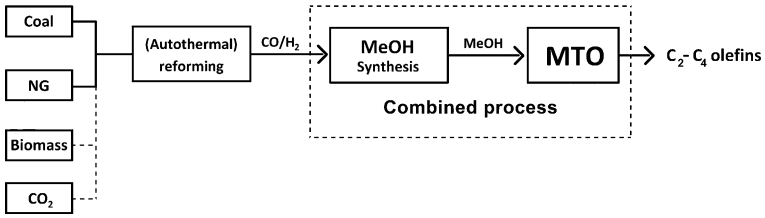


"If I could be a piece of lab equipment, I would be a centrifuge.
The greatest scientific advance of the last decade was 3D printing …"
This and more about Zhiyong Tang can be found on page 7290.

Books

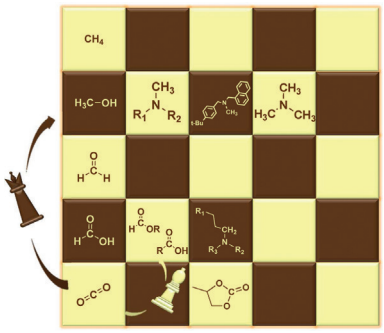
Highlights

Heterogeneous Catalysis

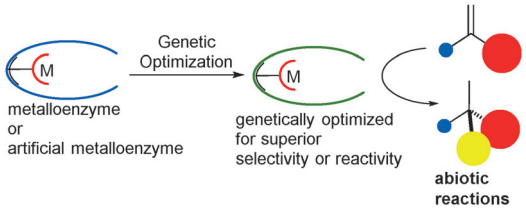


All together now: Combination in a single reactor of the catalysts for converting syngas into methanol and methanol into olefins was recently reported by Cheng et al. This approach considerably simplifies the catalytic conversion of natural gas.

Reviews

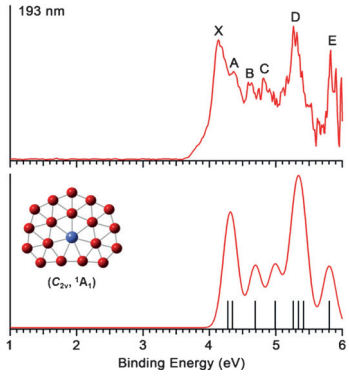


The catalytic gambit: The combined use of CO_2 and H_2 as building blocks in catalytic processes provides access to products ranging from large volume base chemicals to highly functionalized complex molecules. The current state-of-the-art is critically reviewed, highlighting pathways that are in line with "green chemistry" principles and offer the potential to harness renewable energy into the chemical value chain.



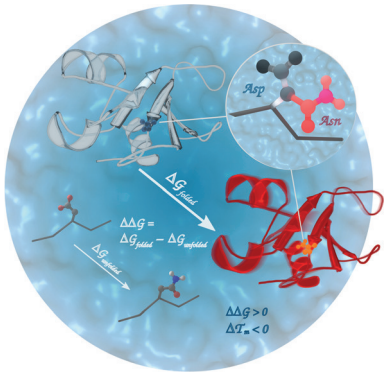
The second row also matters: In contrast to traditional transition-metal catalysts, artificial metalloenzymes can modulate both the first and second coordination spheres, and thus result in novel reactivities. This Review discusses attempts to modulate the second coordination sphere of artificial metalloenzymes through genetic modifications of the protein sequence.

Communications

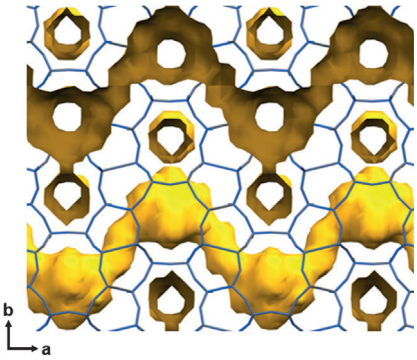


No bending: The CoB_{18}^- cluster was investigated experimentally and theoretically. It is found to be a highly stable and perfectly planar structure consisting of a monovalent Co atom centered in a seven-membered ring.

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.

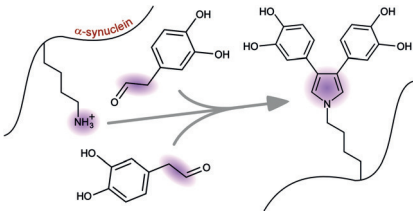


The computational prediction of the changes in protein thermostability upon an amino acid mutation greatly aids protein engineering and design. It is shown that such predictions can be rendered remarkably accurate by means of molecular-dynamics-based alchemical free-energy calculations.

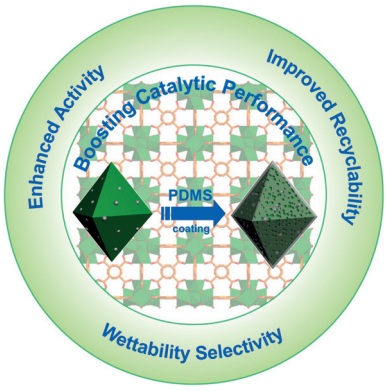


Structure elucidation: The structure of the small-pore zeolite EU-12, which has remained unknown during the past 30 years, was determined by synchrotron powder X-ray diffraction and Rietveld analyses (see picture). EU-12 shows a superior catalytic performance for the dehydration of ethanol.

Amyloid disease: The primary dopamine metabolite, 3,4-dihydroxyphenylacetaldehyde, reacts with α-synuclein Lys residues to form dicatechol pyrrole lysine adducts, which may act as the scaffold for the protein crosslinking observed in dopaminergic cells. The dicatechol pyrrole lysine adducts were characterized by NMR spectroscopy and mass spectrometry.

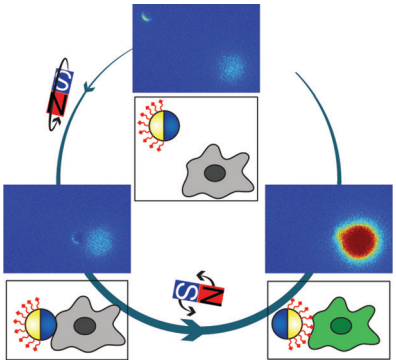


Hydrophobic visions: Surface hydrophobization of Pd/UiO-66, a composite of a metal–organic framework (MOF) and stabilized palladium nanoparticles, was realized using a simple polydimethylsiloxane (PDMS) coating. The resultant Pd/UiO-66@PDMS composite exhibits superior catalytic activity and recyclability compared to pristine Pd/UiO-66, and additional selectivity in sieving reactants with different wettability. This approach is extendable to various Pd-based catalysts.

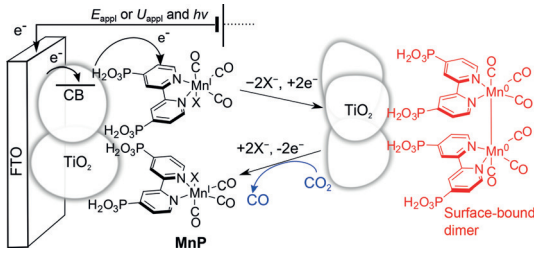


Janus Particles

Janus particles were employed to control T cell activation. The particles were magnetically responsive on one side and displayed ligands for T cell stimulation on the other side. T cell activation was remotely controlled by simultaneously manipulating the rotation and locomotion of the magnetic Janus particles.



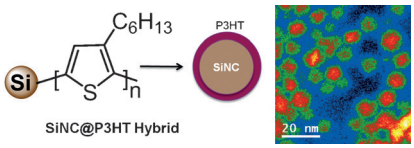
CO_2 Reduction



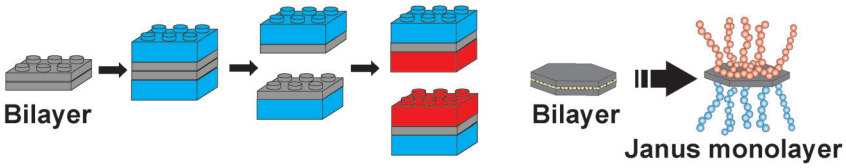
One small step for Mn: A Mn catalyst immobilized on TiO_2 gave electrocatalytic CO_2 reduction with a turnover number of 112. The low overpotential of 420 mV is a result of dimerization of the catalyst on the mesoporous electrode. The heterogeneous hybrid cathode was used in a photoelectrochemical cell enabling solar-driven CO production by a photo-unstable Mn catalyst for the first time.

Hybrid Materials

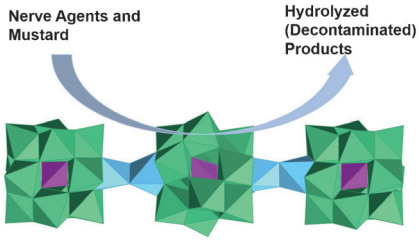
Hybrid functional materials of silicon nanocrystals and poly(3-hexylthiophene) (SiNC@P3HT) consisting of a direct conjugate covalent bond between SiNC and P3HT were developed. Systematic characterization provides evidence of a core–shell structure, enhanced interfacial electron and/or energy transfer between the P3HT and SiNC components, as well as formation of a type-II heterostructure.



Hybrid Materials

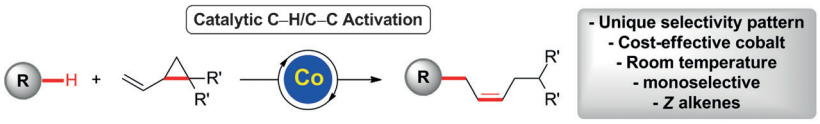


Controlled exfoliation of layered silicate heterostructures into bilayers with unprecedented precision by osmotic swelling gives access to a general method for asymmetrical modification of basal planes. Only two simple steps are needed to obtain Janus-type monolayers as bulk material.



POM against CWAs: A new one-dimensional polymeric polyniobate, $K_{12}[Ti_2O_2][GeNb_{12}O_{40}]$, removes a wide range of chemical warfare agents (CWAs) and their simulants. The transformations are catalytic and proceed effectively under very mild conditions and in the dark.

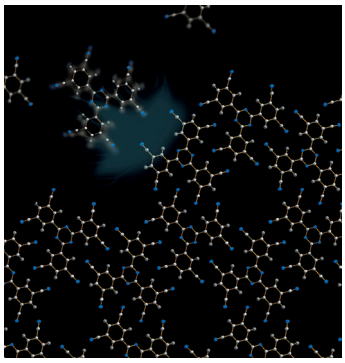
Decontamination



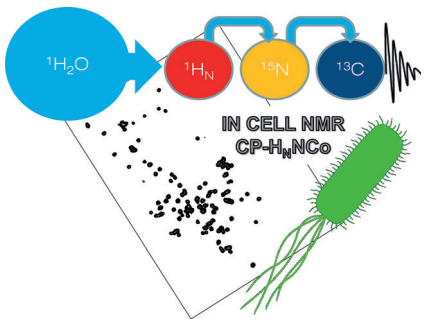
Double activation: Challenging C–H/C–C functionalizations were achieved through the use of cobalt catalysis under exceedingly mild reaction conditions. This method leads to the formation of *Z* alkenes with unique chemo- and diastereoselectivity.

C–H/C–C Activation

Sturdy crystals: The formation of organic-molecule-based superstructures was realized by solid-state conversion of an organic single-crystal. The resultant porous organic framework with 1-dimensional channels showed unusually high thermal stability tolerance to electron-beams.



Porous Crystals

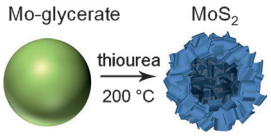


Keep your finger on the pulse: A new pulse sequence combining proton–nitrogen cross-polarization and carbonyl detection is proposed for recording high-resolution, high-sensitivity NMR spectra of IDPs under true physiological conditions. By this method, a high-quality N–CO correlation spectrum was acquired of α-synuclein in bacterial cells at 37 °C.

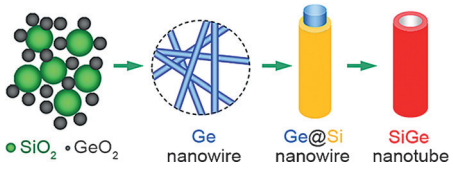
In-Cell NMR Spectroscopy

Nanospheres

Dr Mo: Hierarchical MoS_2 hollow nanospheres are synthesized with a self-templating method from highly uniform Mo–glycerate solid spheres. By sulfidation and annealing, these Mo–glycerate solid spheres can be converted into hierarchical MoS_2 hollow nanospheres. Owing to their unique structures, the hierarchical nanospheres show enhanced electrochemical properties as the anode material for lithium-ion batteries.

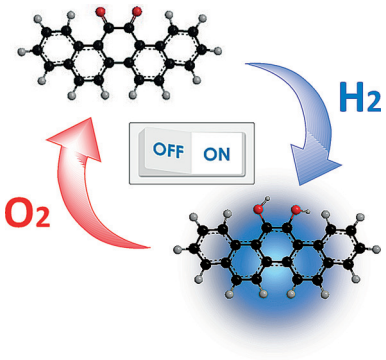


Lithium Storage



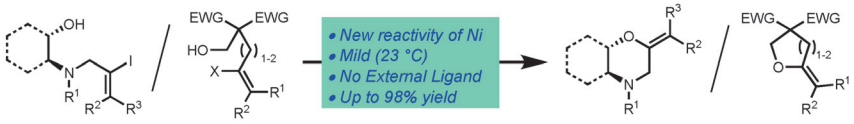
Li likes alloys: Crystalline SiGe alloy nanotubes and hollow particles are synthesized through a one-pot electrolytic process in molten salts. The solid-diffusion process, governed by the nanoscale Kirkendall effect, leads to the formation of internal voids in the SiGe alloy particles. Owing to the unique structural features and desirable composition, the SiGe alloy nanotubes exhibit enhanced lithium-storage performance.

Photoluminescent Materials



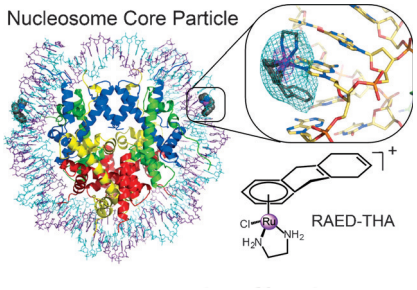
A tale with a twist: Unique redox switching of orthoquinone-containing pentacyclic aromatic compounds was observed upon exposure to H_2 and O_2 in the presence of a sulfur-modified gold-supported palladium nanoparticle catalyst (see picture). Switching between the orthoquinone and the corresponding hydroquinone led to a drastic change in the photoluminescence and color of the system owing to differences in the aromaticity and twist strain of the molecules.

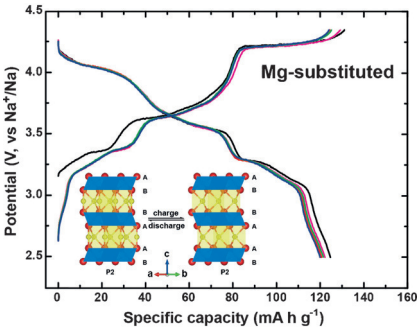
Cross-Coupling



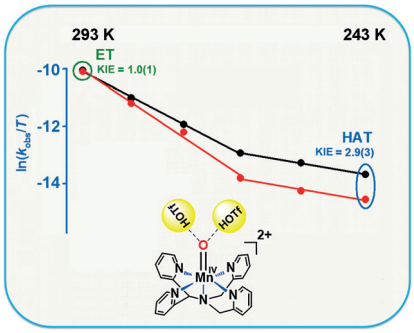
Nickel-O-C-eon: The title reaction between aliphatic hydroxy nucleophiles and tethered vinyl halides provides access to cyclic vinyl ethers in a single step and under exceptionally mild and operationally simple reaction conditions. The exploration of this new reactivity of nickel catalysts can provide further insight into the unique properties and opportunities afforded by nickel catalysts. EWG = electron-withdrawing group.

Binding preferences: Using crystallographic methods and molecular dynamics simulations it was shown that adducts formed by the anticancer agent [(η^6-5,8,9,10-tetrahydroanthracene)Ru(ethylenediamine)Cl][PF_6] on a nucleosome comprise a novel one-stranded intercalation and DNA distortion mode. The adduct dimorphism and DNA topology dependence might contribute to the unusually high cytotoxicity of this anticancer agent.



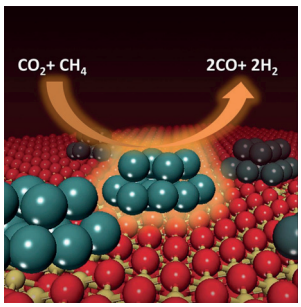


The P2–O2 phase transition in P2-$Na_{0.67}Mn_{0.67}Ni_{0.33-x}Mg_xO_2$ can be effectively suppressed by substituting some of the nickel ions with magnesium. Both the reversible capacity and the capacity retention of this cathode material were thus remarkably improved, and the various phases were characterized by scanning tunneling electron microscopy with atomic resolution.



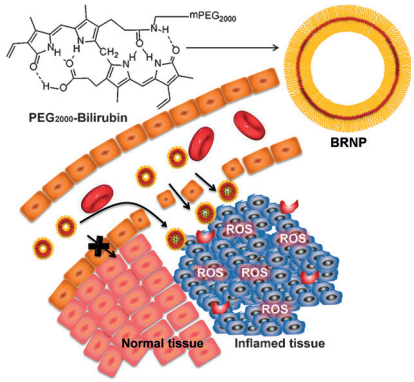
The switchover of the reaction mechanism from electron transfer (ET) to hydrogen-atom transfer (HAT) for a protonated nonheme manganese(IV)–oxo complex was investigated. The switchover occurs in the presence of triflic acid by changing only the reaction temperature in the boundary region between ET and HAT pathways. KIE = kinetic isotope effect; black = mesitylene, red = [D_{12}]mesitylene.

NiCe and dry: Ni-CeO_2 is shown to be highly efficient, stable, and non-expensive catalyst for methane dry reforming at relative low temperatures (700 K). The active phase of the catalyst consists of small nanoparticles of nickel dispersed on partially reduced ceria. Strong metal–support interactions activate Ni for the dissociation of methane.



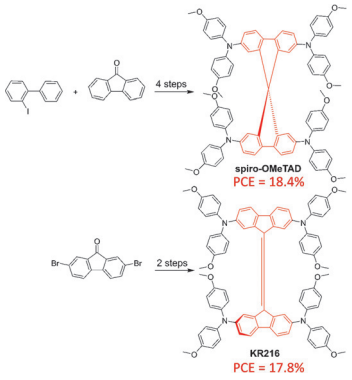
Nanomedicines

Bilirubin, a nanomedicine for inflammatory diseases: Bilirubin, a highly potent anti-inflammatory but extremely water insoluble compound, is converted into nanoparticles by simply introducing PEG. The resultant bilirubin nanoparticles show potential as a nanomedicine in anti-inflammation therapy. ROS = reactive oxygen species, BRNP = Bilirubin nanoparticle.

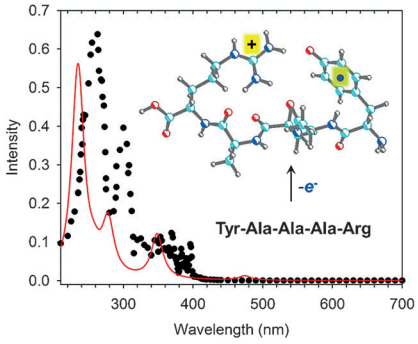


Solar Cells

The hole-transporting material KR216 (4,4′-dimethoxydiphenylamine-substituted 9,9′-bifluorenylidene) reached a photon-to-current efficiency (PCE) of 17.8% in perovskite-based solar cells. A novel material was synthesized using a straightforward two-step procedure from commercially available and inexpensive starting reagents, mimicking the 9,9′-spirobifluorene moiety of the well-studied spiro-OMeTAD.

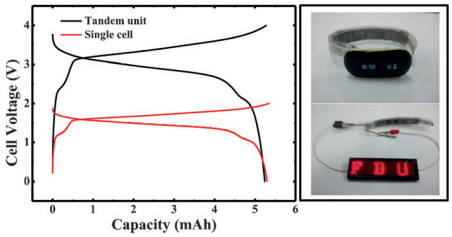


Gas-Phase Chemistry

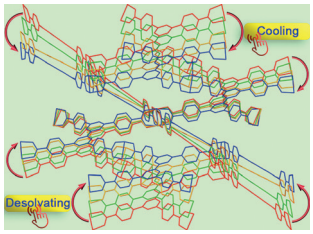


UV/Vis action spectrum: Tyrosine peptides underwent different courses of oxidation by copper(II) ions depending on the position of the tyrosine residue in the peptide sequence. Tyrosine peptide cation radicals were produced by oxidative intramolecular electron transfer in the gas-phase copper complexes.

Lithium-Ion Batteries

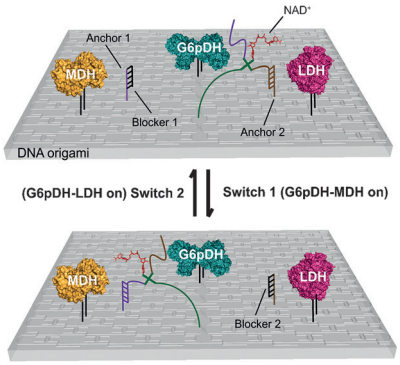


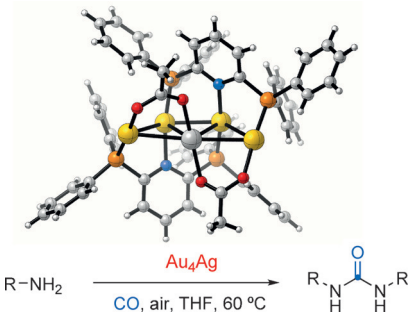
Wearable electronic devices: A wearable aqueous lithium-ion battery based on a spinel $Li_{1.1}Mn_2O_4$ cathode and a carbon-coated $LiTi_2(PO_4)_3$ anode offered a high safety standard and showed excellent flexibility, and a large volumetric energy density.



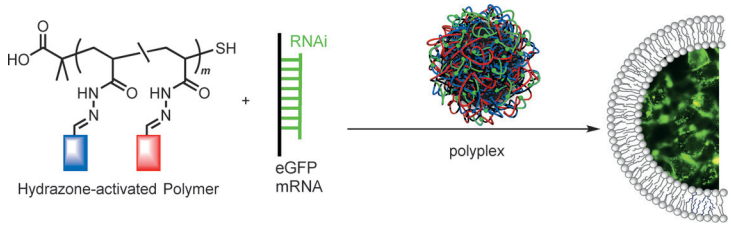
See the shrink: A record high uniaxial positive thermal expansion coefficient of $653.2\times10^{-6}\ K^{-1}$ and large *c*-axial shrinkage of 32.4%, is found for metal–organic framework (MOF) temperature- and solvent-responsive soft crystals. The dynamic process can both be visualized by in situ single-crystal X-ray snapshot analyses. The stimuli-responsive mechanism results from rotations and deformations of the organic linkers.

Artificial multi-enzyme systems with precise and directional control over the enzyme pathway activities are of great significance in bionanotechnology and synthetic biology. A DNA origami system for the directional regulation of the activities of two enzyme pathways (G6pDH–MDH and G6pDH–LDH) through the control of NAD+ substrate channeling by specifically shifting NAD+ between the two enzyme pairs is now reported.



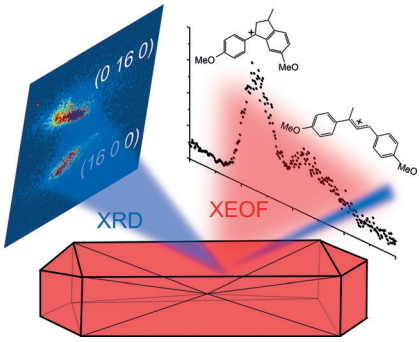


Gold aplenty: The synthesis of tetranuclear gold complexes, a structurally unprecedented octanuclear complex with a planar $[Au^{I}_{8}]$ core, and pentanuclear $[Au^{I}_{4}M^{I}]$ (M = Cu, Ag) complexes is presented. The linear $[Au^{I}_{4}]$ complex undergoes C–H functionalization of carbonyl compounds under mild reaction conditions. In addition, $[Au^{I}_{4}Ag^{I}]$ catalyzes the carbonylation of primary amines to form ureas under homogeneous conditions with efficiencies higher than those achieved by gold nanoparticles.



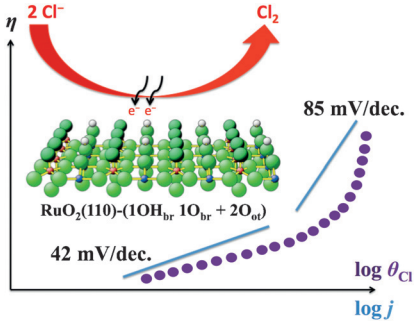
Signed, sealed, delivered: The chemical functionality of a polyhydrazide scaffold was modified by careful choice of cationic (blue box; see picture) and hydrophobic (red) aldehydes to produce amphiphilic vectors for supramolecular polynucleotide delivery.

Chemical Imaging



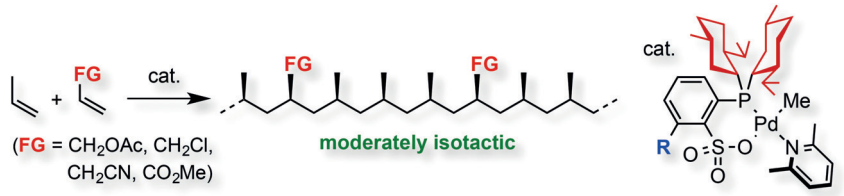
Two worlds in one X-ray shot: The local crystallinity and acid-catalyzed chemistry of a single zeolite crystal were determined by a combination of micro-X-ray diffraction (μ-XRD) and X-ray excited optical fluorescence (μ-XEOF), achieved by using one X-ray beam to excite fluorescent products formed in a zeolite. The intergrowth structure and Al zoning play a decisive role in the degree of dealumination and shape-selective product formation.

Electrocatalysis



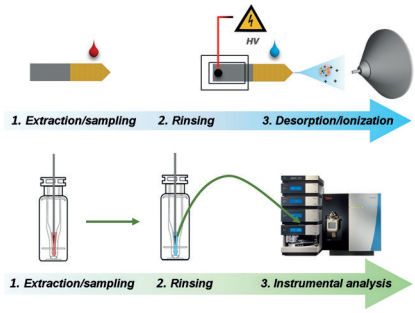
Beyond thermodynamics: An intimate interplay of thermodynamics and kinetics from first principles together with microkinetic modeling allows the microscopic processes of the chlorine evolution reaction over a RuO_2(110) model electrode to be unraveled. This combined approach may provide a general roadmap on how electrocatalytic reactions can be studied to gain unprecedented molecular insight.

Polymerization



Control center: High-molecular-weight polypropylenes can be obtained by using palladium catalysts bearing menthyl-substituted phosphine-sulfonate ligands for the isospecific homopolymerization of propylene or the copolymerization of propylene with polar monomers. The introduction of substituents at the *ortho*-position relative to the sulfonate group favors enantiomorphic site control over chain end control in the chain propagation step.

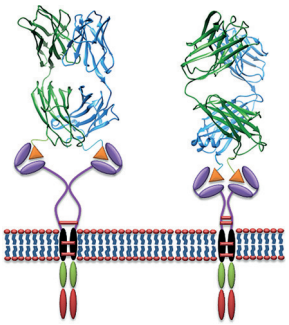
Sample Preparation



Simple sampling: solid-phase microextraction (SPME) devices perform fast extraction/enrichment of target analytes in small sample volumes. Micro-sampling is performed with metal tips coated with a thin layer of polypyrrole (see picture, bottom) or by using thin-coated blade spray (CBS) devices (top). These devices can be coupled with liquid chromatography (LC), or directly to mass spectrometry (MS).

Chemically redesigned DNA, in which all four nucleobases are functionalized (denoted DZA), was used to transfer genetic information in living organisms. Using a gene encoding resistance to the antibiotic trimethoprim, a fully morphed DNA was successfully replicated in vitro and served as a genetic template in vivo.

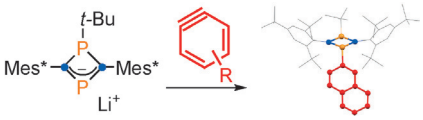
Nucleic Acids



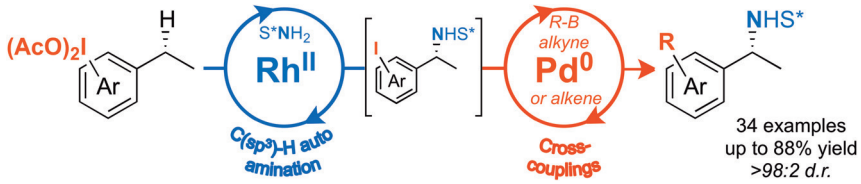
CAR-T control: Chimeric antigen receptor T (CAR-T) cells were engineered to be controlled by exogenous switch molecules. Site-specific incorporation of the small molecule FITC or a short peptide neo-epitope in the anti-Her2 4D5 Fab allowed activation of corresponding switchable CAR-T cells towards Her2-expressing solid tumor cells, and displayed significant anti-cancer effects both in vitro and in vivo.

Cancer Immunotherapy

A P_2romising C_2onstellation: The reaction of a sterically encumbered 1,3-diphosphacyclobuten-4-yl anion with *ortho*-silylated aryl triflates in the presence of fluoride under appropriate conditions afforded the corresponding 1-aryl-1,3-diphosphacyclobutane-2,4-diyls (see scheme). These air-stable open-shell singlet P-heterocycles exhibit considerable electron-donating character and can be used as detectors of hydrogen fluoride.



Phosphorus Heterocycles

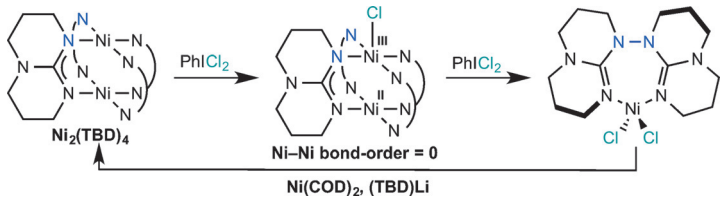


Poly-valent iodine: The design of one-pot reactions involving a catalytic auto C-(sp^3)–H amination followed by Pd-catalyzed couplings has led to polyfunctionalized enantiopure amines. An iodine(III) reagent can thus be used both as an oxidant and a substrate, then as a coupling partner. The overall process reveals iodoarene-derived oxidants to be versatile building blocks in synthesis.

C–H Amination

N–N Bond Formation

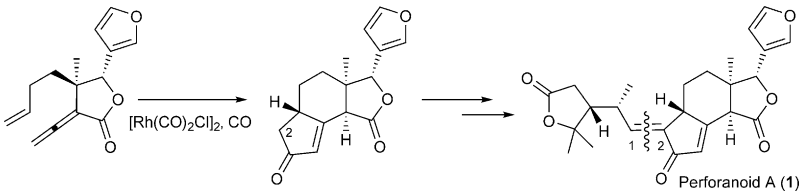
N–N Bond Forming Reductive Elimination via a Mixed-Valent Nickel(II)–Nickel(III) Intermediate



A "paddle-wheel" Ni complex undergoes N–N bond forming reductive elimination under oxidative conditions. The intermediate is a mixed-valent Ni^{II}–Ni^{III} complex with a Ni–Ni bond order of zero.

Total Synthesis

Isolation and Asymmetric Total Synthesis of Perforanoid A

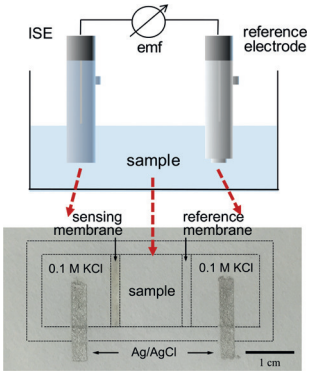


When life gives you limonoids: A novel limonoid, perforanoid A, was isolated, and an asymmetric total synthesis was achieved in 10 steps. The key steps are chiral tertiary aminonaphthol mediated enantioselective alkenylation of an aldehyde to an allylic alcohol, Pd-catalyzed coupling of the allylic alcohol with vinyl ether to form the γ-lactone ring, and cyclopentenone ring formation through a Rh-catalyzed Pauson–Khand reaction.

Analytical Methods

A Disposable Planar Paper-Based Potentiometric Ion-Sensing Platform

Paper-based sensors: Embedding a potentiometric cell into paper brings selective ion sensors into the reach of users with limited resources and training. The paper-based device is simple to use, does not need any pretreatment, and requires only a low sample volume of 20 μL. It can be used to detect clinically relevant ions in biological samples with high sensitivity and reproducibility. ISE = ion-selective electrode.



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